Mild Oxidation of Styrene and Its Derivatives with Ionic Manganese Porphyrin Immobilized in the Similarly Structured Ionic Liquid

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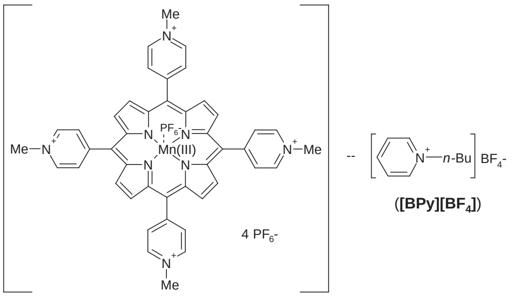
Without the auxiliary involvement of axial ligands and organic solvents, the ionic manganese porphyrin **1c** immobilized in [BPy][BF$_4$] efficiently catalyzed the oxidation of styrene and its derivatives under mild conditions, affording high activity/oxide selectivity and good stability even after 5 recycling uses.

Various oxidations such as epoxidation of olefins and hydroxylation of hydrocarbons with oxygen donors (iodosylarenes, alkylhydroperoxides, hydrogen peroxide, hypochlorites, periodates, etc.) have been catalyzed by metalloporphyrins as model catalysts of cytochrome P450 in homogeneous organic media, in which axial ligands like imidazole or pyridine (derivatives) are required necessarily to activate and stabilize active metal porphyrin species.[1–5] Anyway, the intermolecular self-aggregation due to π–π stacking and the propensity for oxidation led to destruction and difficult recovery of metalloporphyrin in such systems. In order to solve these problems, many heterogeneous methods have been developed to improve metalloporphyrin dispersion, stability and recovery.[6–8]

Ambient ionic liquids (ILs) are not only environmentally benign solvents with unique physical properties, but also liquid and flexible "carriers" of functional units (such as metal complexes, phosphines etc.) through the formation of covalent bond.[9,10] For example, to avoid metal catalyst leaching out of IL system, the efforts have been made to enhance the solubility/miscibility of the metal catalysts through grafting electron-donor ligands into ILs which can coordinate with metal centers,[11] or incorporating imidazolium/pyridinium tags into a metal complex.[12] Herein, we report the oxidation of styrene and its derivatives with iodosylbenzene (PhIO) oxidant catalyzed by Mn porphyrin with pyridinium tag **1c** which was immobilized in ambient IL of [BPy][BF$_4$], without auxiliary involvement of the axial ligand and the volatile organic solvent.

The catalyst of manganese tetrakis-(*N*-methyl-4-pyridinium)porphyrin hexafluorophosphate ([Mn^{III}T(*N*-Me-4-Py)**P**]-[PF$_6$]$_5$, **1c**) was miscible in *N*-butylpyridinium tetrafluoroborate ([BPy][BF$_4$]) due to the ionic nature and the similar skeletons, building up the multi-component IL system which was composed of four types of ions ([Mn^{III}T(*N*-Me-4-Py)**P**]$^{5+}$, [BPy]$^+$, [PF$_6$]$^-$, [BF$_4$]$^-$) (Scheme 1). In open air, the oxidation of styrene and its derivatives catalyzed by **1c** with PhIO was carried out (Table 1). Under mild reaction conditions (30 °C) and without auxiliary involvement of axial ligands, the isoelectronic products of styrene oxide and phenylacetaldehyde were obtained in 86% and 10% yield, respectively, without C=C bond cleavage. Even the concentration of catalyst **1c** was decreased to 0.005 mol %, the styrene conversion of 41% was obtained, with turnover rate of 8200/h^{-1} (see Supporting Information).[16] The oxidation of styrene derivatives showed that with the electron-withdrawing group in para-position of styrene, the selectivities for oxides were remarkable (100%). If the substituting groups possess electron-donor nature (–Cl, –Br, –CH$_3$), the increased electron-density at the α-C of C=C bond resulted in the formation of benzaldehyde through the oxidation of side-chain cleavage. While for the substrates (Entries 7 and 8) with an internal C=C bond, the epoxides were the only products, implicating the facial access of the substrate to oxomanganese(V) porphyrin domain.[13] For the olefins with saturated alkyl group, such as 1-hexene, 1-chloropropene, cyclohexene, etc., the poor conversions were observed mainly because of the mass-transfer limitation, ascribing to the immiscibility between the substrates and the conjugated multi-component IL of **1c**–[BPy][BF$_4$].

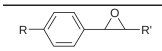
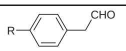
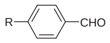
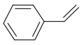
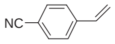
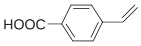
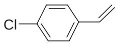
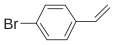
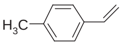
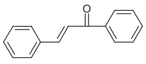
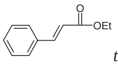
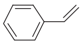
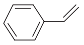
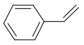


(**1c**)

Scheme 1. Multi-component IL system: **1c** immobilized in [BPy][BF$_4$].

Upon completion of the reaction, the solution was extracted with diethyl ether leaving behind the light purple IL which could be reused for next pass (The leaching of Mn in organic phase was beyond the limit of ICP detection.) The results in Table 2 indicated that the activity and the stability maintained quite well even after 5 runs (the fresh, 96% conv.; the fifth run, 71% conv.). Anyway in the third run, the selectivity of styrene oxide and phenylacetaldehyde varied greatly. In order to clarify the derivation of the various oxidized products, the purchased (±)-styrene oxide (Johnson Matthery, 98%) was used to replace styrene in the fresh **1c**–[BPy][BF$_4$] system and the used one in the presence of PhIO, respectively (see Supporting Information).[16] It was found that there was no any conversion of (±)-styrene oxide to phenylacetaldehyde, ruling out the possibility of the subsequent isomerization of styrene oxide to phenylacetaldehyde. The formation of phenylacetaldehyde maybe resulted from the induced Mn^{IV}–oxo derivative of **1c** which was considered to react with the substrate by a radical mechanism giving rise to increased the amount of aldehydes relative to that of oxide. The decreased catalytic activity of **1c** was mainly attributed to the degradation of the porphyrino ring, but not from the derivation of Mn^V=O species to other Mn^{III,IV,V}–oxo species, which was only responsible for the selective distribution of

Table 1. Oxidation of styrene and its derivatives catalyzed by **1c** in [BPy][BF_4][a]

No.	Olefin	Catalyst	Solvent	Axial Ligand	Conversion /%[c]	Selectivity/%[d]		
								
1		**1c**	[BPy][BF_4]	—	96 (1 h)[b]	90	10	0
2		**1c**	[BPy][BF_4]	—	97 (3 h)[b]	100	0	0
3		**1c**	[BPy][BF_4]	—	98 (3 h)[b]	100	0	0
4		**1c**	[BPy][BF_4]	—	95 (4 h)[b]	57	35	9
5		**1c**	[BPy][BF_4]	—	91 (4 h)[b]	65	29	6
6		**1c**	[BPy][BF_4]	—	91 (2 h)[b]	57	40	4
7	 *trans-*	**1c**	[BPy][BF_4]	—	96 (4 h)[b]	100	0	0
8	 *trans-*	**1c**	[BPy][BF_4]	—	71 (4 h)[b]	100	0	0
9		**1c**	CH_3CN	pyridine	71 (1 h)	74	26	0
10		**2b**	CH_3CN	pyridine	98 (1 h)	77	23	0
11		**2b**	[BPy][BF_4]	—	48 (1 h)	73	27	0

[a]Cat. 1.6 μmol (0.4 mol %), substrate 400 μmol, PhIO 600 μmol, pyridine 130 μmol, [BPy][BF_4] 2 mL, reaction temperature 30 °C. [b]Reaction time was indicated in parentheses. [c]Based on GC analysis with 1-dodecane as internal standard. [d]Based on GC analysis according to normalization method.

Table 2. The recycling uses of **1c**–[BPy][BF_4] for oxidation of styrene[a]

Run	Conv./%[b]	Sel./%[c]		
		Styrene oxide	Phenylacetaldehyde	Benzaldehyde
1	96	90	10	0
2	92	90	10	0
3	87	60	40	0
4	79	17	82	1
5	71	0	99	1

[a]**1c** 1.6 μmol; styrene 400 μmol; [BPy][BF_4] 2 mL; reaction temperature 30 °C; reaction time 1 h; PhIO (400 μmol) which was added per pass. [b]Based on GC analysis with 1-dodecane as internal standard. [c]Based on GC analysis according to normalization method.

oxygenated products.[14]

It is noteworthy that the recycling uses of **1c** in [BPy][BF_4] showed that the destruction (aggregation and oxidation) of metalloporphyrin was suppressed dramatically, compared to that of the conventional neutral manganese(III) tetrakis(4-pyridyl)-porphyrin ([$Mn^{III}T(4\text{-}Py)P$], (**2b**), see Supporting Information).[16] Due to the common ionic nature, the similar conjugated feature, and the repulsive force between anions and cations, the π–π interaction between **1c** and [BPy][BF_4] counteracted the self-aggregation of porphyrin, which favored the stability and dispersion of **1c** in [BPy][BF_4]. The pyridinium cations in **1c** made the electron density at meso-carbons decreased, improving the oxidation tolerance of metalloporphyrin.[5] Meanwhile, [BPy][BF_4] not only acts as the ideal solvent for **1c** and the conjugated substrates, but also plays the role of axial ligand to **1c** like pyridine derivative, favoring stability and activation of the active oxomanganese(V) porphyrin species.[5,14,15]

In summary, the multi-component IL in Scheme 1 has been developed as an efficient and recyclable catalytic system for oxidation of styrene and its derivatives compared to the conventional **2b** system (see Supporting Information).[16] The good activity and the improved stability of **1c** in [BPy][BF_4] were dependent on a number of factors that included the dual roles of [BPy][BF_4] as the axial ligand and the solvent, the decreased electron density at meso-carbon of porphyrin **1c**, and the restrained π–π stacking of porphyrin self due to the ionic nature and the similar conjugated feature between **1c** and [BPy][BF_4].

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.