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Ion Exchange Catalysis in Oxidation of Organic Compounds with KMnO₄

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ABSTRACT

The oxidation of organic compounds under ion exchange resin (IER) catalysis by KMnO₄ has been studied in CH₂Cl₂ under reflux conditions. Secondary aliphatic and aromatic alcohols are converted to ketones, alkyl arenes and sulfides oxidized to corresponding ketones and sulfones, respectively, and thiols undergo oxidative coupling reactions to give disulfides. The experimental procedure is simple and products are easily isolated in good yields.

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A wide range of organic synthesis have been accomplished using the acidic and basic forms of ion exchange resin as catalyst.^[1-4] The advantages in using insoluble ion exchange resins in catalysis are that they are readily available and corrosion problems involving apparatus and plant are minimal. In addition, it can be easily removed from reaction mixture and the bulk reaction volume is not contaminated with acid or base or their related fragments.

Very recently, we reported the oxidation of organic compounds under solvent free ion exchange resin catalysis by NaBrO₃ at room temperature.^[5] In continuation of our studies on the application of KMnO₄ in oxidation of organic compounds,^[6–11] we wish to report ion exchange resin catalysis in oxidation of organic compounds by means of KMnO₄ as a simple methodology and an efficient oxidant system under heterogenous conditions in CH₂Cl₂.

As indicated in Sch. 1, secondary aliphatic and aromatic alcohols are converted into the corresponding ketones in good yields (Table 1). Carboxylic acids are obtained in comparable yields from the oxidation of primary alcohols (Entries 9 and 10).

As can be seen from the Table 2, alkyl arenes are converted into the corresponding carbonyl compounds in good yields under ion exchange catalysis by KMnO₄. The products are identical to those obtained under heterogeneous conditions where the KMnO₄ is supported on CuSO₄.5H₂O and alumina,^[11] however, the reaction times are reduced from a few days to a few hours. As indicated in Sch. 2, the reaction displays an interesting selectivity for compound containing oxygen as part of a cyclic side chain. It is interesting that toluene and *p*-xylene readily oxidized with this system to corresponding acids (Entries 10 and 11).

Alkyl and aryl sulfides are converted into the corresponding sulfones in good yields (Table 3). This is a highly useful reaction for the preparation of sulfones which are important intermediates in the synthesis



Scheme 1.

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Table 1. Oxidation of alcohols to carbonyl compounds by KMnO₄/IER in CH₂Cl₂ under reflux conditions.

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Entry	Reactant	Product	Time (h)	Yield (%)	M.p. of 2,4-DNP (°C)	M.p. of product (°C)
1	OH	$\bigcup \overset{\circ}{\bigcup}$	4	91	255–257 (258) ^a	40–42 (42) ^b
2	ОН		4.15	93	249–250 (250) ^a	_
3	ОН	o	4.30	94	145–148 (148) ^a	_
4	ОН		4.30	93	160–162 (162) ^a	-
5	OH		5	92	55–58 (58) ^a	_
6	ОН		5	93	104–106 (106) ^a	_
7	ОН	Î.,	4.30	92	115–117 (117) ^a	_
8	ОН		4.15	93	142–144 (144) ^a	_
9	ОН	ОН	4.15	95	_	130–133 (133) ^b
10	ОЧ	ОН	4	94	_	108–110 (107–111) ^b
11	ОН	No Reaction	5	_	_	_

^aFrom ref. ^[18]

^bFrom ref. ^[19]

of many organic compounds.^[12] The observation that benzyl phenyl sulfide and dibenzyl sulfide are oxidized to the corresponding sulfones indicate that the reactions proceed by way of an oxygen transfer mechanism (Sch. 3). If the reactions involved electron transfer instead of oxygen transfer, substantial amounts of benzaldehyde would have been formed.[13,14]

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Table 2. Oxidation of alkyl arenes to carbonyl compounds by KMnO₄ /IER in CH₂Cl₂ under reflux conditions.

Entry	Reactant	Product	Time (h)	Yield (%)	M.p. of 2,4-DNP (°C)	M.p. of product (°C)
1			5.30	91	248–250 (250) ^a	_
2			5.45	93	190–191 (191) ^a	_
3	$\bigcirc\bigcirc$		7	95	_	127 (127) ^b
4	$\bigcirc \bigcirc \bigcirc$	\bigcup°	7	93	253–256 (258) ^a	41–42 (42) ^b
5		C C	6.30	94	_	72–74 (71–74) ^b
6			7.30	93	_	172–174 (174) ^b
7			7.30	94	280–282 (283) ^a	(81–84) 84 ^b
8	$\bigcirc \bigcirc \bigcirc$		8.15	90	_	(47–49) 48 ^b
9	\bigcirc		5.45	92	198–200 (200) ^a	_
10	\bigcirc	ОН	3	90	_	120–122 (121) ^b
11	Н	одон	6	93	_	Sub. (Sub.) ^b
		ő				

^aFrom ref. ^[18] ^bFrom ref. ^[19]

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Aromatic and aliphatic thiols are also oxidatively coupled under these conditions in relatively high yields (Table 4, Sch. 4). The reaction times are shorter than those reported for the corresponding heterogeneous reactions.^[15]

EXPERIMENTAL

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Melting points were determined in open capillaries using an oil-bath and are uncorrected. IR spectra were as neat films or as KBr pellets on a Shimadzu 470 spectrometer. ¹H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with CDCl₃ as solvent and Me₄Si as an internal standard. Yields reported refer to isolated products or 2,4-dinitrophenylhydrazone derivatives (2,4-DNP) of the carbonyl compounds.^[16,17] The ion exchange resin, Rexyn 101 H, was obtained from the Fisher Scientific Company.

TYPICAL PROCEDURE

Oxidation of Cyclohexanol with KMnO₄/IER

Cyclohexanol (0.101 g, 1 mmol) was dissolved in CH_2Cl_2 (30 mL) and placed in a round-bottomed flask. Finely grounded KMnO₄ (1 g) and IER (1 g) were added and the mixture was stirred at reflux conditions for 4.30 h. The product was filtered through sintered glass and residue washed with CH_2Cl_2 (20 mL). The solvent was evaporated to give a product (0.93 mmol, 93%). The melting point of the 2,4-DNP derivative was 160–162°C (Lit.^[18] 162°C).

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reflux conditions.						
Entry	Reactant	Product	Time (h)	Yield (%)	M.p. or B.p. (°C)	
1	C S	o o o	5	85	85–87 (86–86.5) ^a	
2	S →	o o o	5	94	152–155 (154–155) ^b	
3	Br	Br	6	89	97–100 (97) ^b	
4	O ₂ N	O ₁ N ^O S ^O	6	90	133–137 (133–137) ^b	
5	∧ s ∧)	o S	7	91	128–129 (128–130) ^b	

Table 3. Oxidation of sulfides to sulfones by KMnO₄/IER in CH₂Cl₂ under 4;+;

3	Br S O O	6	89	97–100 (97) ^b
4		6	90	133–137 (133–137
5		7	91	128–129 (128–130)
6		5.30	87	144–146 (146) ^b
7	s s	5.30	88	151–155 (155) ^b
8	s os	4	95	35–40 (28–45) ^c
9	Solution of the second	4	88	45–46 (45–46) ^b
10	$\begin{bmatrix} C_8 H_{17} \end{bmatrix}_2^S \begin{bmatrix} C_8 H_{17} \end{bmatrix}_2^{SO_2}$	4	91	74–76 (74) ^b

^aFrom ref. ^[21] ^bFrom ref. ^[19] ^cFrom ref. ^[22]



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Entry	Reactant	Product	Time (h)	Yield (%)	M.p. or B.p. ($^{\circ}$ C)
1	SH	CH ₂ S ₂	2.30	96	71–73 (71–72) ^a
2	SH	[3	94	127–130 (125–130) ^b
3	∕SH		2.30	94	91–93 (92.5) ^b
4	∽~~ ^{SH}	~~~ ^{\$-\$} ~~~	2.15	95	113–116 (114–115) ^c
5	C ₈ H ₁₇ SH	$\left[C_{8}H_{17}\right]S_{2}$	2.45	96	185–188 (186–188) ^d

Table 4. Coupling of thiols by KMnO₄/IER in CH₂Cl₂ under reflux conditions.

^aFrom ref. ^[20]

^bFrom ref. ^[23]

^cFrom ref. ^[24]

^dFrom ref. ^[19]

 $2 \text{ R SH} \xrightarrow{\text{KMnO}_4/\text{IER}}_{2.15-2.45 \text{ h}, 94-96\%} \text{ R S-S R}$ Scheme 4.

Oxidation of Indan with KMnO₄/IER

Indan (0.118 g, 1 mmol) was dissolved in CH_2Cl_2 (30 mL) and placed in a round-bottomed flask with a magnetic stirrer. Finely grounded KMnO₄ (1 g) and IER (1 g) was added and the mixture was stirred at reflux conditions and the extent of reaction monitored by using of TLC. After 7 h, analysis of the liquid phase by TLC indicated complete conversion to 1-indanone. The product was filtered through sintered glass and residue washed with CH_2Cl_2 (20 mL). The solvent was evaporated to give a product (0.93 mmol, 93%) which showed only one TLC spot and 2,4-DNP derivative of indanone melted at 253–256°C (Lit.^[18] 258°C).

Oxidation of Dibenzyl Sulfide with KMnO₄/IER

Dibenzyl sulfide (0.214 g, 1 mmol) dissolved in CH₂Cl₂ (30 mL), was placed in a round-bottomed flask equipped with a magnetic stirrer.

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Finely grounded KMnO₄ (1 g) and IER (1 g) was added and the mixture was stirred at reflux conditions and the extent of reaction monitored by using of TLC. After 5.30 h, analysis of the liquid phase by TLC indicated complete conversion to dibenzyl sulfone. The product was filtered through sintered glass and residue washed with CH₂Cl₂ (20 mL). The solvent was evaporated to give a product (0.88 mmol, 88%) which produced only one TLC spot and melted at 151–155°C (Lit.^[19] 155°C).

Oxidation of Benzyl Thiol with KMnO₄/IER

Benzyl thiol (0.124 g, 1 mmol) was dissolved in CH_2Cl_2 (30 mL) and placed in a round-bottomed flask with a magnetic stirrer. Finely grounded KMnO₄ (1 g) and IER (1 g) added. The mixture was stirred at reflux conditions and the extent of reaction monitored by use of TLC. After 2.30 h, analysis of the liquid phase by TLC indicated complete conversion to dibenzyl disulfide. The product was filtered through sintered glass and residue washed with CH_2Cl_2 (20 mL). The solvent was evaporated to give a product (0.96 mmol, 96%) which produced only one TLC spot and melted at 71–73°C (Lit.^[20] 71–72°C).

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