SHORT PAPER

Cation exchange resin supported oxidation of alkylbenzenes and olefins using potassium permanganate[†]

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Rapid and efficient oxidation of alkylbenzene side chains at the benzylic positions as well as oxidative cleavage of olefins with potassium permanganate in presence of solid polymeric cation exchange resins in good yields is reported.

Potassium permanganate ($KMnO_4$) is an oxidising agent used in organic chemistry, is one of the most versatile and vigorous of the commonly used oxidants, and has been extensively employed in acid, alkaline and neutral medium. The oxidation products can be glycols, hydroxy ketones, diketones, epoxides or cleavage products dependent on the reaction conditions. Unfortunately, the conditions under which these reactions take place are not sharply defined and mixture of products are often obtained.[1] To induce some sort of selectivity and control, several modified means of carrying out permanganate oxidations have been reported which involve solubalisation of permanganate in organic solvents with the help of phase transfer catalysts,[2] crown ether,[3] or preparing quarternary ammonium salts.[4]

One recent development that has significantly expanded the scope of this reagent is its use in presence of inorganic supports. The effectiveness of a particular support material for a given reagent and reaction is likely to be the result of combition of factors including surface area, porosity, acidity, basisity as well as the crystalline or amorphous nature of the material. The polymeric support provides a particular reaction environment capable of enhancing the reactivity of many reagents and moreover, turns out to be very profitable in the working up, which becomes reduced to a mere filtration. One major and only recently appreciated advantage of supported reagents is their potential as environmentally friendly alternatives to corrosive, wasteful and difficult to dispose of conventional reagents.[5]

Regan and Koteel[6] have reported that various types of molecular sieves, silica and K-catalysts can easily be impregnated with $KMnO_4$ and the resulting reagents are useful for alcohol oxidations. Hydrated copper sulfate supported $KMnO_4$ oxidises secondary alcohols to ketones,[7] however alkenes are converted into α-diketones or α-hydroxy ketones when treated with $KMnO_4$ and copper sulfate pentahydrate in presence of t-butyl alcohol.[8] $KMnO_4$ impregnated on silica gel is reagent of choice for the cleavage of ethylenic double bond to get acids,[9] while alkenes when treated with $KMnO_4$ in presence of moist alumina ends up into corresponding aldehydes or ketones.[10] Moreover, simple addition of certain supports to a reaction mixture can have a dramatic effect on reaction rate as the *in situ* mixing of support (silica gel) and reagent ($NaBH_4$) in the reduction of nitrostyrene.[11] Oxidation of alkylbenzene side chains at the benzylic positions using $KMnO_4$ supported on alumina and copper sulfate has been reported[12] to produce corresponding alcohols and ketones. However in these oxidations the reaction times are quite long (few days).

In continuation of our studies regarding the applications of cation exchange resins,[13] we have found that commercial cation exchange resins without any modification are found to be very useful in oxidations with $KMnO_4$. Despite the failure in preparation of an impregnated reagent using cation exchange resin and $KMnO_4$, we were successful in carrying out the oxidations just by mixing the resins with $KMnO_4$ in a suitable solvent system.

Here we present out results on the oxidation of olefins under very mild conditions with $KMnO_4$, in presence of cation exchange resins (H+ form) to afford the corresponding aldehydes or ketones in high yields and not the acids which are usual products in aqueous medium[1] or when the support material is silica gel.[9] Also we report the oxidations of alkylbenzene side chains under similar reaction conditions in which the products are alcohols if the benzylic carbon is tertiary and ketones if it is secondary, in excellent yields. The alkyl sidechain oxidations are significantly more selective under our reaction conditions than permanganate alone, where carbon-carbon bond cleavage occurs. The reaction times are also short (0.5 to 8 h). Another observation is that the oxidations carried out using potassium permanganate in presence of *p*-toluene sylfonic acid instead of cation exchange resin, are found to proceed much slowly. This indicates that the role of cation exchange resin is not just to provide protons. The reactions are performed using batch technique by stirring an excess of cation exchange resin (H+ form), the olefin or alkylbenzene and finely powdered $KMnO_4$ in a mixed solvent system t-butyl alcohol and dichloromethane at room temperature. Products are isolated by removal of the spent reagent system by filtration, drying over anhydrous Na_2SO_4, evaporation of the solvent and purification by column chromatography. The products are identified either by comparison with authentic samples or by NMR and IR spectroscopy. The use of cation exchange resins in the oxidation of olefins and alkylbenzenes with $KMnO_4$ has not been reported so far.

Oxidation of cinnamic acid was studied in detail by changing solvents, resins and stoitiometric quantities of $KMnO_4$. Solvents like chlorinated hydrocarbons, actone and diethylether are found to be equally effective, the reaction in benzene is sluggish while no reaction takes place when hexane is used as a solvent. Moreover, systematic examination of eight different support systems (Table 1) has established that Tulsion T-40 is by far the most suitable for the oxidation of olefins and superior to others in handling and general experimental simplicity. Similarly Tulsion T-42 is the resin of choice of the oxidation of diphenyl methane, so it has been used for all the oxidations of alkylbenzenes.

Experimental

All melting points are uncorrected. IR spectra are recorded on a Perkin-Elmer Infrared 599-B spectrophotometer model using NAC1 optics. ^{1}H NMR are run in $CDCl_3$ solution on a Bruker AC-200 NMR spectrophotometer operating at 200Hz using tetramethylsilane as an internal standard. Mass spectra are recorded on Finnigan Mat 1020C Mass spectrophotometer at 70eV. TLC is performed using precoated aluminium sheets with silica gel $60F_{254}$, Merck, Germany. For column chromatography ACME silica gel 100–200 mesh size is used. Methylene chloride is freshly distilled over clacium hydride. Cation exchange resins are procured from Thermax (India). Ltd. Pune. All oxidation products are known compounds and the identity is confirmed by comparison of their physical and spectral data.

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[†] This is a Short Paper, there is therefore no corresponding material in
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Table 1 Oxidation of cinnamic acid by permanganate- cation exchange resins

Entry	Resin[a]	Time (min)	Remarks[b]
1	Tulsion T-40[c]	30	Wet (52% moisture)
2	Amberlyst-15	20	Dry
3	Amberlyte IR-100	30	Dry
4	IR-120	35	Dry
5	Tulsion T-42	15	Dry
6	Indion-130	35	Dry
7	Zeocarb-225	45	Dry
8	CXO-18[c]	90	Wet (52% moisture)

[a]Entries 1–7 are strongly acidic cation exchange resins (H^{+} forms) having matrix structure with styrene divinylbenzene copolymer having sulfonicacid groups. Entry No. 8 is in a weakly acidic cation exchange resin (H^{+} form) having matrix structure with styrene divinylbenzene copoluymer having carboxylic acid functional groups. [b]While conducting the reactions with dry resins, equal quantity of water is added to the reaction mixture. [c]Since the distribution of water is uniform throughout the polymer matrix, the reactions carried out using this resin are smooth, associated with batch to batch consistency and the work-up is more convenient, hence in general Tulsion T-40 resin is preferrred even though the time required for complete conversion is a little more as compared to some of the dry resins.

Table 2 Oxidative cleavage of olefins

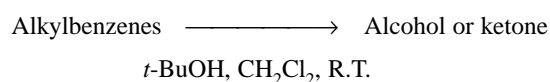| Entry	Reactant	Reaction time (h)	Product (%yield)[a]
1	Cinnamic acid	0.5	Benzaldehyde (86%)
2	Cyclooctene	4	1,8-Octanediol (73%)[b]
3	β-Pinene	3.5	Nopinone (65%)
4	trans-Stilbene	3	Benzaldehyde (82%)
5	α-Methyl styrene	4	Acetophenone (81%)

[a]Isolated yields, product identity is confirmed by comparison with ^{1}H-NMR and IR spectra of authentic compounds. [b]The yield is based on the quantity of 1,8-Octanediol obtained by subsequent reduction of the dialdehyde intermediate with sodium borohydride.

Typical procedure for oxidative cleavage of olefins: KMnO$_4$ (2.37g, 15 mmol) is added to a suspension of Tulsion T-40 resin (4g), t-butyl alcohol (4ml), *trans*-stilbene (900mg, 5mmol) in dichloromethane (25ml) in lots during 5 min. The reaction mixture was stirred at room temperatuire for 3h, filtered and dried over anhydrous Na$_2$SO$_4$. After removing the solvent, the product obtained shows single spot on TLC and found to have identical spectral properties with benzaldehyde (870mg, 82%).

Typical procedure for oxidation of alkylbenzenes: KMnO$_4$ (0.948g., 6mmol) is added to a suspension of Tulsion T-42 resin (2g), t-butyl alcohol (4ml), water (1ml), tetralin (264mg, 2mmol) in dichloromethane (20ml) in lots during 10 min time. The reaction mixture was stirred at room temperature for 4 h, filtered and dried over anhydrous Na$_2$SO$_4$. After removing the solvent, the product obtained is purified by column chromatography to get α-tetralone (263mg, 90%).

The oxidation reactions are performed using different substrates and our results are summarised in Tables 2 and 3. The salient featues of these oxidations is the use of only three mole equivalents of KMnO$_4$ and the reaction times are also quite shorter (few hours) than previously reported where the duration of the reaction is extended to few days.

In conclusion the cleavage of olefins and selective oxidation of alkylbenzenes at the benzylic position with KMnO$_4$ in presence of commercially available cation exchange resins (without any modification) can be carried out in very good yields

Tulsion T-40, KMnO$_4$

Olefins ⎯⎯⎯⎯⎯⎯→ Aldehydes or ketones

t-BuOH, CH$_2$Cl$_2$, RT
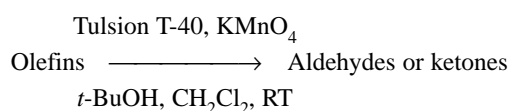
Scheme 1

Tulsion T-42, KMnO$_4$

Alkylbenzenes ⎯⎯⎯⎯⎯⎯→ Alcohol or ketone

t-BuOH, CH$_2$Cl$_2$, R.T.

Scheme 2

Table 3 Oxidation of alkylbenzenes

Substrate	Product	KMnO$_4$ (eq.)	Time (h)	Yield[a] (%)
Diphenylmethane	Benzophenone	3	3	92
Ethylbenzene	Acetophenone	3	4.5	86
Tetralin	a-Tetralone	3	4	90
Isobutylbenzene	Isopropylphenyl ketone	3	5	88
Cumene	2-Phenyl-2-propanol	3	4	82
Phenethylalcohol	Acetophenone	3	0.5	94
Benzoin	Benzil	6	7	76[b]
Stilbene-1,2-diol	Benzil	6	8	75[b]
Phenylacetic-acid	Benzoyl-formicacid	6	No	reaction[c]
Menthol	methone	6	No	reaction

[a]Isolated yields, product identity is confimed by comparison with [1] H-NMR and IR spectra of authentic compounds.[b] About 10–15% of benzoin is recovered in the column chromatopraphic purification. [c]Only 60% of the starting material is recovered back.

with the use of only three mole equivalents of KMnO$_4$, under simple reaction conditions and in very short time. The oxidation products can be isolated very easily in relatively pure form. The oxidation of olefins and alkylbenzenes with KMnO$_4$ in presence of cation exchange resins has been reported for the first time. The fact that the manganese ions in these reactions remain firmly bound to the resin after the reaction, may be valuable in preventing environmental pollution. These results suggest that activiation of KMnO$_4$ in presence of cation exchange resins may provide an attractive synthetic alternative to related techniques such as phase transfer, use of quarternary ammonium salts or inorganic supports. In view of its optional simplicity, efficiency, the method described above will hopefully prove to be of wide synthetic use.

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