

Polymer-Supported Reagents. Mild and Efficient Method of Oxidation of Alcohols*

F. Shirini¹, M. Dabiri², S. Dezyani², and F. Jalili³

¹ Department of Chemistry, Faculty of Science, Guilan University, P.O. Box 1914, Rasht, 41355 Iran
e-mail: shirini@guilan.ac.ir

² Department of Chemistry, Shahid Beheshti University, Tehran, Iran

³ Merck Trading, P.O. Box 15745-653, Tehran, Iran

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Abstract—A mild and efficient procedure has been proposed for the oxidation of alcohols to the corresponding carbonyl compounds using quaternary ammonium Dowex 1-X8 resin in which chloride ions have been replaced by permanganate ions MnO_4^- (DMn).

Although numerous methods for the oxidation of alcohols to the corresponding carbonyl compounds are known [1–6], in the general case the problem cannot be regarded as solved completely. The main disadvantages of the known procedures include difficulties in the preparation of necessary reagents and treatment of reaction mixtures. Insoluble polymer-supported reagents are convenient from the practical viewpoint for solving many problems in organic synthesis [7–9]. A polymeric support provides a specific reaction medium which favors enhanced reactivity of a number of reagents and facilitates treatment of reaction mixtures: the products can readily be isolated by simple filtration. For example, anion exchangers were successfully used in the C-alkylation of phenols [10], O-alkylation of carboxylate ions [11], and synthesis of alkyl and aralkyl fluorides [12]. Polymeric thioanisole was shown to be effective [13] in the Corey oxidation of alcohols [14]. The efficiency of polymer-supported reagents was demonstrated using fairly sensitive compounds as substrates, in particular in the oxidation of some intermediate products in the synthesis of prostaglandins [13]. However, the entire procedure was fairly laborious, and specially prepared polymers were required.

In the present communication we report on a simple preparation of a convenient polymeric reagent for oxidation of alcohols on the basis of commercially available anion exchanger. The oxidant was obtained as follows: 5 g of Dowex 1-X8 (Cl^- form, 20–50 mesh)

was added under stirring to a solution of 3 mmol of KMnO_4 in 40 ml of water. After 3 h, chloride ions were completely replaced by MnO_4^- . The product was washed in succession with water and acetone and dried for 15 min at 50°C under reduced pressure. The IR spectrum of the modified resin contained the following absorption bands, ν , cm^{-1} : 725 w, 900 m (MnO_4^-), 1036 w, 1063 m, 1112 m, 1622 s, 1789 m [15]. In order to determine the capacity, a mixture of 0.5 g of the modified resin and 30 ml of 2 N H_2SO_4 was stirred for 1 h. A known excess of a standard More salt solution was added, and the mixture was stirred until the dark resin color disappeared completely. The unreacted More salt was titrated using a standard solution of potassium permanganate, and permanganate equivalent of the obtained Dowex 1-X8/ MnO_4^- (DMn) was calculated (0.6 mmol of MnO_4^- per gram of the resin).

The polymer-supported reagent showed a high efficiency in the oxidation of alcohols to the corresponding carbonyl compounds which were formed in 50–95% yield (see table). The oxidation procedure was as follows: a mixture of 1 mmol of alcohol and 5 mmol DMn (taking into account its capacity) in 10 ml of acetonitrile was heated under reflux with stirring over a period indicated in table. The mixture was filtered to remove the resin, and the product was isolated by evaporation of the filtrate. In all cases, the products contained neither traces of the corresponding acids nor other impurities. In some cases, the reaction was not complete, and a part of the initial alcohol was recovered from the reaction mixture. The resulting carbonyl compounds were identified by comparing

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Oxidation of alcohols to carbonyl compounds with permanganate-modified Dowex 1-X8 anion exchanger (DMn and DMnP)

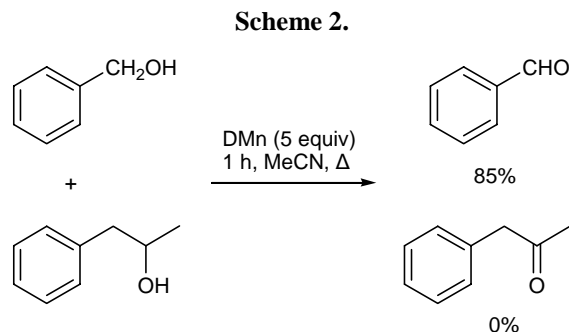
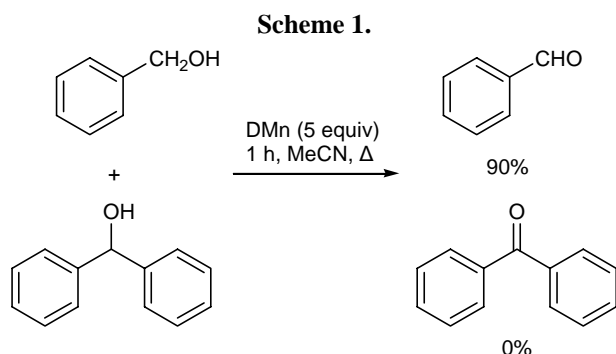
Substrate	Product	DMn			DMnP		
		oxidant-to-substrate molar ratio	time, h	yield, ^a %	oxidant-to-substrate molar ratio	time, h	yield, ^a %
Benzyl alcohol	Benzaldehyde	5	1	90	4	0.5	92
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	5	2	85	4	0.5	90
3-Methoxybenzyl alcohol	3-Methoxybenzaldehyde	5	2	90	4	0.5	85
2-Methoxybenzyl alcohol	2-Methoxybenzaldehyde	5	5	70	4	1.5	80
4-Bromobenzyl alcohol	4-Bromobenzaldehyde	5	2	80	4	0.5	95
4- <i>tert</i> -Butylbenzyl alcohol	4- <i>tert</i> -Butylbenzaldehyde	5	6.5	90	4	0.5	95
Diphenylmethanol	Benzophenone	5	15	85	4	1	80
3-Phenyl-1-propanol	3-Phenylpropanal	5	2.5	50	4	1	75
1-Phenyl-2-propanol	Acetophenone	5	5	50	4	1	50
3-Phenyl-2-propen-1-ol	Cinnamaldehyde	5	8.5	52	4	3	90
Benzoin	Benzil	5	8.5	95	4	1.5	92
4,4'-Dimethylbenzoin	4,4'-Dimethylbenzil	5	2	55	4	2	95
Furoin	Furil	5	5	90	4	5	90

^a Yield of the isolated product.

their melting points (or boiling points and refractive indices) and IR and ¹H NMR spectra with those of authentic samples.

The rate of oxidation of aliphatic and sterically hindered benzyl alcohols with DMn is so low that the reagent can be used for selective oxidation. Examples are the oxidation of benzyl alcohol in the presence of diphenylmethanol and 1-phenyl-2-propanol as shown in Schemes 1 and 2.

It should be noted that the reaction time and the selectivity, as well as the oxidant-substrate molar ratio, decrease when powdered DMnP is used (Dowex 1-X8,



Cl⁻, 100–200 mesh; see table). The polymer-supported reagent can readily be regenerated by washing with 25 ml of 5 N H₂SO₄ and subsequent treating with potassium permanganate according to the above procedure. Its efficiency did not change after three successive oxidation-regeneration cycles.

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