SYNTHETIC COMMUNICATIONS, 31(19), 2885–2889 (2001)

POLYMER SUPPORTED REAGENTS: OXIDATIVE SELECTION BETWEEN BENZYLIC ALCOHOLS

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ABSTRACT

Dowex 1-X8, as a quaternary ammonium resin, on which $Cl^- \Rightarrow Cl^-$ is replaced by dichromate and bisulfate ions (DDB), can be used as a stable and efficient oxidizing reagent for oxidative selection between benzylic alcohols according to their structures.

There has been an incessant interest in the development of new Cr(VI) reagents for the effective oxidation of organic substrates, especially under mild aprotic conditions. That is why a number of monomeric and polymer-supported Cr(VI) reagents have been reported in the literature,[1] of which Jones' reagent,[2] $CrO_3/N^+Bu_4HSO_4^-$,[3] *n*-butyltriphenylphosphonium dichromate,[4] pyridinium chlorochromate,[5] pyrazinium dichromate,[6] ferric dichromate,[7] polyvinylpyridinium chlorochromate[8] and dichromate,[9] polyvinylpyridine-supported ferric dichromate,[10] polyethyleneimine-supported

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silver dichromate[11] and supported quaternary ammonium complex chromates[3] are examples.

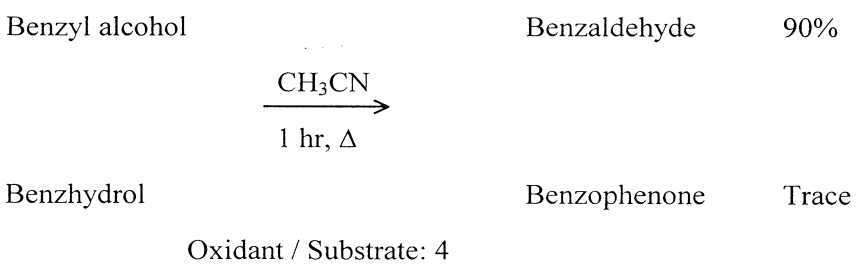
However, most of the monomeric and some of the polymeric reagents mentioned above suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of preparation and the need for a large excess of the reagent. Thus a milder, more selective and inexpensive reagent is still desirable.

In this communication we report that Dowex 1-X8, in which $Cl^- \Rightarrow Cl^-$ is replaced by $Cr_2O_7^{2-}$; and HSO_4^- (DDB), is able to oxidize benzyl alcohols directly to their corresponding carbonyl compounds in high yields (Table 1). Overoxidation of the product was not observed by this method.

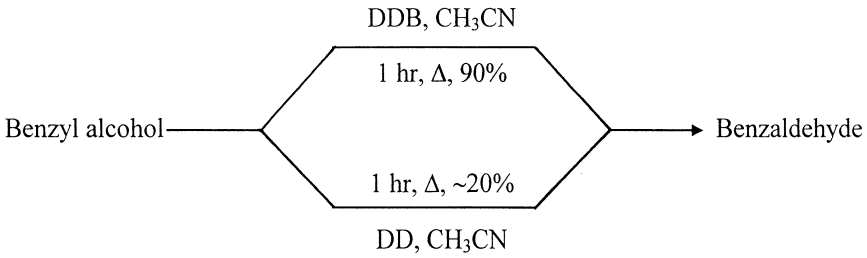
Sterically hindered benzyl alcohols do not undergo oxidation with this reagent. Therefore, this methodology shows selectivity and is suitable for oxidative selection amongst benzyl alcohols according to their structures. This is exemplified by the competitive reaction between benzyl alcohol and benzhydrol (Scheme 1).

Table 1. Oxidation of Benzylic Alcohols with DDB in Refluxing Acetonitrile

Entry	Substrate	Oxidant Substrate	Product	Reaction Time (h)	Yield (%)
1	Benzyl alcohol	4	Benzaldehyde	1	90
2	4-Chlorobenzyl alcohol	4	4-Chlorobenzaldehyde	1.2	85
3	4-Bromobenzyl alcohol	4	4-Bromobenzaldehyde	1.5	80
4	4-Methylbenzyl alcohol	4	4-Methylbenzaldehyde	1.5	92
5	1-Phenyl ethanol	4	Acetophenone	3.5	90
6	1-Naphthyl ethanol	4	1′-Acetonaphthone	9	90
7	4-Phenoxybenzyl alcohol	6	4-Phenoxybenzaldehyde	7.5	82



Scheme 1.



Scheme 2.

Table 2. Comparison of Some of the Results Obtained by the Oxidation with DDB(1), with Some of Those Reported by Chromic Acid on Amberlyst A-26(2), Crosslinked Polyvinyl-Pyridine-Supported Ferric Dichromate (3) and Pyrazinium Dichromate (4)

		(Oxidant/Substrate) (h) (Yield (%))			
Entry	Substrate	(1)	(2)	(3)	(4)
1	Benzyl Alcohol	(4)(1)(90)	(13)(1)(98)	(1)(1.5)(35)	(1)(3.5)(73)
2	1-Phenyl Ethanol	(4)(3.5)(90)	–	(1)(1)(35)	(1)(3.5)(91)

It should be noted that the progress of the reaction depends on the presence of HSO_4^- in the reagent. This can be shown through comparing the oxidation of benzyl alcohol by bisulfate-containing reagent (DDB) with the oxidation of benzyl alcohol in the absence of bisulfate (DD) by the reagent (Scheme 2). These results show the key role of HSO_4^- in the oxidation process, which may be related to the requirement for acidic media, needed in the oxidation of different alcohols with sodium or potassium dichromates.[12,13]

In order to show the oxidizing ability of this reagent we have compared some of the results with some of those reported in the literature[5,10,14] (Table 2).

Recycling of DDB can be accomplished by using a simple washing-reactivation procedure in which the spent reagent is washed repeatedly with 2 M sodium hydroxide and 2 M hydrochloric acid solution. After regeneration, Dowex 1-X8 in chloride form is added to the solution of CrO_3 in H_2SO_4 in order to reactivate the reagent. A sample of the reagent passed through three reaction cycles with no loss of oxidizing capacity and only a slight decrease in reaction rate.

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EXPERIMENTAL

All products were characterized through comparison of their spectral and physical data with those of the known samples.[15] The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. Dowex 1-X8 (Cl^- form, 20–50 mesh) and other chemicals were purchased from Merck. Products were separated and purified by different chromatography techniques, and were also identified by the comparison of their mp, IR and NMR spectra, bp, refractive index with those reported for the authentic samples. The capacity of the reagent was determined by atomic absorption technique and titration method.

Preparation of DDB: To a solution of CrO_3 (0.35 g, 3.5 mmol) in 0.5 M H_2SO_4 (40 mL),[16] Dowex 1-X8 (5 g) was added and the mixture stirred for 0.5 h at room temperature. The resulting dark-orange resin was filtered and washed with acetone (2×20 mL) and diethylether (2×5 mL) and was finally dried *in vacuo* at 50°C for 0.5 h. The infrared spectrum of the dry reagent showed bands at 930 and 765 cm^{-1}, characteristic of dichromate ion and bands at 820, 847, 877, 1045, 1180, 1220, 1420 and 3250 cm^{-1}, characteristic of bisulfate ion.[17]

The capacity of the reagent was determined to be 0.25 mmol $Cr_2O_7^{2-}$ and 1.5 mmol $H_2SO_4^-$ per gram of the resin.

General procedure for the oxidation of benzylic alcohols with DDB: To a solution of benzylic alcohol (1 mmol) in acetonitrile (8 mL), DDB (4–6 mmol based on capacities) was added and refluxed while stirred for 1–9 h. Progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and filtered being followed by repeated washing with acetonitrile (2×5 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compound from good to high yields (Table 1).

Regeneration of Dowex 1-X8 in its Cl^- form: To an aqueous solution of NaOH (2 M, 20 mL) the spent reagent (2 g) was added and the mixture was stirred for 12 h. The suspension was filtered and washed repeatedly with a solution of hydrochloric acid (2 M) and finally with water. The precipitate was dried *in vacuo* at 80°C for 6 h to give the original quaternary ammonium resin characterized by its IR spectrum.

ACKNOWLEDGMENT

We are thankful to Guilan University Research Council for the partial support of this work.

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Received in the UK December 8, 1999

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