

## Note

### Solid phase deoxygenation of oximes to the corresponding carbonyl compounds using bromate exchange resin

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Bromate exchange resin (BRER) prepared by a simple elution technique has been used for deoxygenation of oximes to the corresponding carbonyl compounds in good yields in biphasic condition.

**Keywords:** Bromate, oxidation, solid phase, deoxygenation, bromate exchange resin (BRER)

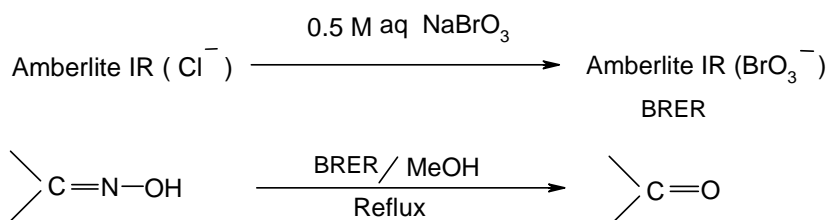
Ion exchange resins are known to be good supports for reagents and catalysts in organic synthesis<sup>1</sup>. Among the advantages of supported reagents in organic synthesis are easy work-up procedure, mild reaction conditions, site specific reactions and high turnover. Supported reagents are also environment friendly<sup>2-6</sup>.

Recently, the use of Bromate Exchange resin (BRER) as an oxidizing agent for the oxidation of aldehydes to carboxylic acids<sup>7</sup> and of alcohols and benzyl halides to the corresponding carbonyl compounds has been reported in biphasic condition<sup>8</sup>. An important observation was that primary alcohols were oxidized only to the aldehydes and over-oxidation to the carboxylic acid was not observed. In continuation of these investigations, herein is reported the use of BRER for the deoxygenation of oximes to the corresponding carbonyl compounds in biphasic condition.

Oximes are crystalline compounds and are used for the isolation, purification and characterization of the parent carbonyl compounds<sup>9,10</sup>. Besides protecting a carbonyl group<sup>11</sup>, oximation gives the product carbonyl oxime which can be used as intermediates for the preparation of nitriles<sup>12</sup>, of amides *via* the Beckmann rearrangement or to activate the carbonyl group<sup>13</sup>. Considering that the oximes can be prepared from non carbonyl precursors and from compounds having active methylene groups by reported procedure<sup>14,15</sup>, deoxygenation becomes a very important procedure not only for the regeneration of the parent carbonyl but also for the conversion of compounds of the type  $Z_1-CH_2-Z_2$  to  $Z_1-CO-Z_2$  where  $Z_1$  and  $Z_2$  are electron withdrawing groups, thus leading to new methods for the preparation of carbonyl compounds from hydrocarbon sites.

The classical acid catalyzed hydrolysis of oximes as a method of deoxygenation proved to be unsatisfactory, especially when acid sensitive functional groups are present in the molecule<sup>16</sup>. Some methods have been reported for the oxidative deoxygenation of oximes notable among them are 2,6-DCPCC<sup>17</sup>, TMSCl (Ref. 18),  $Mn(OAc)_2$  (Ref. 19), dimethyloxirane<sup>20</sup>, 3-carboxypyridinechlorochromate<sup>21</sup>, and *t*-butylhydroperoxide<sup>22</sup>. Despite great improvements reported, these methods suffer from the multiple disadvantages of using harsh reaction conditions, costly reagents and elaborate recovery procedures. In addition to the recent work for deoxygenation using tetra-*n*-alkylammonium bromates<sup>23</sup>, herein is reported another alternative method using BRER for oxidative deoxygenation of oximes to the corresponding carbonyl compounds in excellent yield (**Scheme I**). Thus oximes were subjected to deoxygenation reaction and the results are summarized in **Table I**.

It is noteworthy that unlike other methods of deoxygenation, the present method does not result in



**Scheme I**

**Table I** — Deoxygenation of oximes corresponding to the carbonyl compounds

	Substrate	Product	Reflux Time (hr)	Yield (%)	Obs	m.p. °C Lit
1			2	89	48	48
2			3	85	115	117
3			2	80	107	106
4			2	90	47	47
5			1.5	86	74	73
6			1.5	90	42	44
7			3	86	74	71
8			2.5	90	55	58
9			1.5	86	177	179
10			1	90	96	95

any over-oxidation of aldehydes to the carboxylic acid and the formation of by products were not observed. Camphor oximes could be converted to camphor (entry 9) and  $\alpha,\beta$ -unsaturated oximes were deoximated without oxidation of the double bond (entry 8). Besides acid and base sensitive groups remain unaffected.

In conclusion, BRER prepared by a simple elution technique has been used for the deoximation of the oximes to the corresponding carbonyl compounds. Experimental conditions are mild and simple along with easy work-up procedure and the products are obtained in high yield.

### Experimental Section

All reagents and solvents were purified by methods reported in literature<sup>24</sup>. The anion exchange resin used was Amberlite IR 400 (Cl<sup>-</sup> form) according to Rohm and Hass specification. Melting points of the products were taken in open capillaries and are uncorrected. IR spectra were recorded in KBr pellets in a Perkin-Elmer 1600 FT-IR spectrometer. <sup>1</sup>H NMR were recorded in EM 390, 90 MHz spectrometer in CDCl<sub>3</sub> with TMS as internal standard.

### Conversion of Amberlite IR 400 (Cl<sup>-</sup>) to BRER

BRER was prepared by eluting the anion exchange resin several times with an aqueous 0.5 molar solution of NaBrO<sub>3</sub>. The BRER was washed thoroughly with distilled water and dried. Effervescence observed on addition of HCl to the resin beads indicated the presence of the bromate ions. The amount of loading was reported<sup>7</sup> to be 0.9 milliequivalent of BrO<sup>-</sup> per gram of resin.

### General procedure for the oxidative deoximation of oximes with BRER

To 0.01 mole of the oxime dissolved in 100 mL of methanol was added 15 g of the BRER and the solution was stirred at reflux temperature. The progress of the reaction was monitored by TLC on prepared silica gel-G plates using authentic samples of the starting material and the target compounds as references. A mixture of ethyl acetate-hexane (1:9) was used as eluent. After completion of the reaction, the resin beads were filtered off, the solvent was removed by distillation under reduced pressure and the solid obtained was dissolved in minimum volume of ethanol and poured into ice cold water. The product

was washed several times with water. The products were identified by determining their m.p., <sup>1</sup>H NMR and IR spectra and comparing them with those obtained from authentic samples.

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