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**METHYLAMMONIUM CHLOROCHROMATE ADSORBED  
ON ALUMINA: A CONVENIENT AND EFFICIENT REAGENT  
FOR CLEAVAGE OF CARBON-NITROGEN DOUBLE  
BONDS UNDER NON-AQUEOUS CONDITION**

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**Abstract:** Methylammonium chlorochromate adsorbed on alumina is an easily prepared and stable reagent. With this reagent oximes and *p*-nitrophenylhydrazones are converted to their corresponding carbonyl compounds in good yields.

Derivatives of carbonyl compounds such as oximes and *p*-nitrophenylhydrazones are highly crystalline and very useful for the characterization and purification of carbonyl compounds. Regeneration of carbonyl compounds from their derivatives under mild condition is an important process in synthetic organic chemistry.

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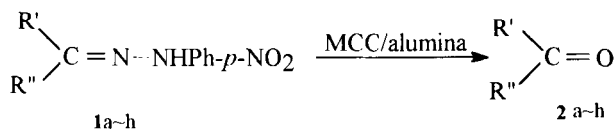
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The classical method for the cleavage of oximes to aldehydes and ketones include acid hydrolysis which is not suitable for acid sensitive compounds<sup>1</sup>. Several oxidative deoxygenation methods have been developed which have been found some advantages over the classical hydrolysis method<sup>2-11</sup>. Little attention has been paid to the oxidative cleavage of *p*-nitrophenylhydrazones and only a few reports are available dealing with the conversion of the derivatives to their corresponding carbonyl compounds<sup>12</sup>.

In this communication we wish to report that methylammonium chlorochromate adsorbed on alumina (MCC/alumina), a stable yellow-orange solid, is able to perform oxidative transformation of organic nitrogen compounds in suitable solvent. This reagent is easily prepared by additional a weighed amount of alumina to a solution of methylammonium chlorochromate in water and rotary evaporation to dryness. This oxidizing agent is stable and may be stored for months without losing its activity. Our experiments show that oximes are converted to their corresponding aldehydes and ketones in moderate yields. Further oxidation of aldehydes to their carboxylic acids are not observed. In contrast, deoxygenation using PCC suffers from long reaction time(12-94h) and low yields<sup>2</sup>. Hydrogen peroxide-PCC system is not suitable for aldoximes and overoxidation products are usually produced<sup>3</sup>. *p*-Nitrophenylhydrazones are also transformed to their carbonyl compounds in dichloromethane with high yields. Carbonyl derivatives of 2,4-dinitrophenylhydrazine remain intact in the reaction mixture under the same reaction conditions.

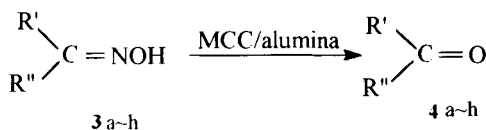
In summary, MCC/alumina is a convenient and efficient reagent for converting oximes and *p*-nitrophenylhydrazones to their corresponding carbonyl compounds. Oxidation of other functional groups with this reagent is under investigation.


Scheme 1



- |   |   |
|---|---|
| a: R' = R'' = Ph  | b: R' = Ph, R'' = CH <sub>3</sub>                                 |
| c: R', R'' = -(CH <sub>2</sub> ) <sub>4</sub>                               | d: R' = -(CH <sub>2</sub> ) <sub>5</sub> -                        |
| e: R' = C <sub>2</sub> H <sub>5</sub> , R'' = C <sub>2</sub> H <sub>5</sub> | f: R' = <i>p</i> -CH <sub>3</sub> OPh, R'' = H                    |
| g: R' = Ph, R'' = H   | h: R' = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> , R'' = H |

Scheme 2



- |  |   |
|--|---|
| a: R' = Ph, R'' = CH <sub>3</sub>  | b: R', R'' = -(CH <sub>2</sub> ) <sub>5</sub> -             |
| c: R' = R'' = Ph   | d: R' = <i>p</i> -O <sub>2</sub> NPh, R'' = CH <sub>3</sub> |
| e: R' = <i>o</i> -HOPh, R'' = H  | f: R' = PhCH=CH, R'' = H                                    |
| g: R' = HO-  , R'' = H | h: R' = <i>p</i> -CH <sub>3</sub> OPh, R'' = H              |

## Experimental

### Preparation of methylammonium Chlorochromate Adsorbed on Alumina

To a solution of chromium trioxide (20g,0.2mol) in water (50ml) is added methylammonium chloride (14g,0.2mol) over 15 min at 40 °C . The mixture is cooled until a yellow-orange solid forms and reheated to 40 °C to give a solution. Alumina (200 mesh) is then added to the solution with stirring at 40 °C . After evaporation on a rotary evaporator, the orange solid was dried in vacuum at 50 °C for 1h. The reagent may be kept for several months in air at room temperature without losing its activity.

Table . Oxidative Cleavage of Carbon-Nitrogen Double Bonds with MCC/alumina

Substrate	Solvent	Oxidant/ substrate	Temp.(°C)	Time (h)	Yields(%) <sup>a</sup>
1a	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	5	98
1b	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	3.5	96
1c	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	6	85
1d	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	4	80
1e	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	3.7	78
1f	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	3.6	93
1g	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	3	75
1h	CH <sub>2</sub> Cl <sub>2</sub>	1.5	35~40	3.3	68
3a	<i>cy</i> -C <sub>6</sub> H <sub>12</sub>	1.6	58~60	3	76
3b	<i>cy</i> -C <sub>6</sub> H <sub>12</sub>	1.6	58~60	2	70
3c	<i>cy</i> -C <sub>6</sub> H <sub>12</sub> +ether	1.6	60	3.5	61
3d	C <sub>6</sub> H <sub>6</sub>	1.6	58~60	3	57
3e	<i>cy</i> -C <sub>6</sub> H <sub>12</sub> +ether	1.6	50~52	2	60
3f	C <sub>6</sub> H <sub>6</sub>	1.6	44~45	2	55
3g	<i>cy</i> -C <sub>6</sub> H <sub>12</sub>	1.6	45~48	2	55
3h	<i>cy</i> -C <sub>6</sub> H <sub>12</sub> +ether	1.6	50~52	2	53

a. Yields were based on 2,4-dinitrophenylhydrazone derivative identified by melting points and the infraed spectra.

#### General Procedure for The Oxidation of Oximes or *p*-Nitrophenylhydrazones with MCC/alumina

Fit a three-necked flask with a condenser, thermometer and magnetic stirrer. Place 2 mmol of oximes or *p*-nitrophenylhydrazones and 20 ml of solvent. To the solution suitable amount of MCC/alumina is added in portion with stirring. The mixture is stirred for additional 2~6h at suitable temperature. The progress of the reaction is followed by GLC. The reaction mixture is filtered, and the solid material is washed with ether several times. The combined filtrate is evaporated to furnished the product which is isolated as a 2,4-dinitrophenylidrazone.

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