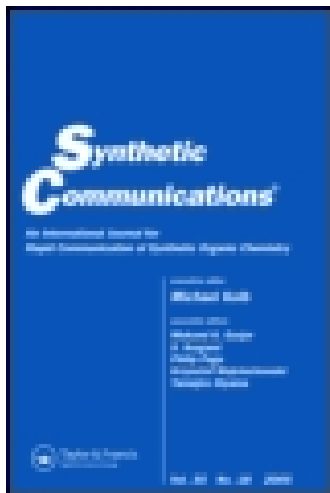


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### Silica Gel Supported Chromium Trioxide: An Efficient Reagent for Oxidative Cleavage of Oximes to Carbonyl Compounds under Mild Condition

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**SILICA GEL SUPPORTED CHROMIUM TRIOXIDE: AN EFFICIENT REAGENT FOR OXIDATIVE CLEAVAGE OF OXIMES TO CARBONYL COMPOUNDS UNDER MILD CONDITION**

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**Abstract:** A facile, efficient oxidative deblocking of aldoximes and ketoximes to their corresponding aldehydes and ketones have been achieved by using silica gel supported chromium trioxide.

Regeneration of carbonyl compounds from their oximes is an important reaction because oxime serves as an efficient protective group for aldehydes and ketones, and these are extensively used for the purification of carbonyl compounds. Since, many valuable reactions have been developed to directly prepare mono oximes of di-carbonyl compounds by nitrosation of mono-carbonyl compounds (Barton reaction)<sup>1</sup>, an efficient deoximation method would be immensely useful. Various methods available for this task, such as acid catalyzed hydrolysis<sup>2-3</sup>, reductive

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deoximation<sup>4-5</sup> and oxidative deoximation<sup>6-7</sup>, still have some difficulties like long reaction time or need of expensive reagents.

In last two decades, utility of chromium (VI) reagents for oxidative deoximation has been tested. However, these methods do have some disadvantages such as long time required (12 - 94 hrs) for deoximation with pyridinium chlorochromate<sup>8</sup>, low yield (35 %) of deoximated products with pyridinium chlorochromate - hydrogen peroxide and formation of oxidative product benzoic acid 35 %<sup>9</sup>, and moderate yields by triethylammonium chlorochromate<sup>10</sup>. We have recently reported the preparation of silchrom, and its utility for the oxidation of various alcohols<sup>11</sup>, aromatization of 1,4-dihydropyridines<sup>12</sup>, and also solid state deoximation of oximes under microwave irradiation<sup>13</sup>. However solution phase reactions or reactions with solid dispersed in liquid media are much easier to scale up. So we thought it necessary to examine the reaction in such condition. We report here an oxidative cleavage of oximes by using new, nonpolluting and inexpensive silica gel supported chromium trioxide oxidant (silchrom).

The mixture of the oxime, and silchrom was gently heated to about 70-75°C in solvents like toluene, benzene, ether or ethylene dichloride to give the corresponding aldehydes and ketones in good yields. All the solvents gave identical results. In case of ketoxime, the starting material got consumed in less than 2.5 hrs and only the corresponding ketone was observed (TLC). Deoximation of aldoximes required slightly longer reaction time. Over-oxidation products, carboxylic acids were observed only in the cases of deoximation of oximes of cinnamaldehyde and 4-nitrobenzaldehyde. Other oximes underwent deoximation without acid contamination. In order to demonstrate the scope of above method, we succeeded in obtaining 1,2-diketones in high yield from corresponding mono oximes.

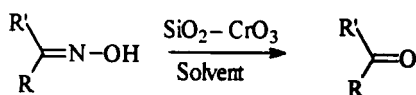


Table: Optimized results of deoximation using silchrom

Entry No.	Oximes	Reaction Time (hrs)	Products <sup>a</sup>	Yield %
1	Benzophenoneoxime	2	Benzophenone	89
2	4,4'-Dichlorobenzophenoneoxime	2	4,4'-Dichlorobenzophenone	90
3	Acetophenoneoxime	2.30	Acetophenone	92
4	2,4-Dimethylacetophenoneoxime	2.30	2,4-Dimethylacetophenone	91
5	4-Bromoacetophenoneoxime	2.30	4-Bromoacetophenone	97
6	4-Hydroxyacetophenoneoxime	2.30	4-Hydroxyacetophenone	84
7	4-Methylacetophenoneoxime	2.30	4-Methylacetophenone	82
8	2-Bromobenzaldoxime	3	2-Bromobenzaldehyde	73
9	3-Bromobenzaldoxime	3	3-Bromobenzaldehyde	86
10	4-Nitrobenzaldoxime	3	4-Nitrobenzaldehyde	67 <sup>b</sup>
11	4-Cyanobenzaldoxime	3	4-Cyanobenzaldehyde	76 <sup>b</sup>
12	Cinnamaldehyde oxime	5	Cinnamaldehyde	72
13	Cyclohexanone oxime	3	Cyclohexanone	91
14	2-Acetylthiophene oxime	4	2-Acetyl thiophene	64 <sup>b</sup>
15	2-Thiophenealdehydeoxime	3	2-Thiophenealdehyde	75 <sup>b</sup>
16	1-Oximino-1-phenyl-2-propanone	4	1-Phenyl-1,2-propanedione	83 <sup>c</sup>
17	2-Oximino-2-phenyl-1-propanone	4	1-Phenyl-1,2-propanedione	80 <sup>c</sup>
18	Diacetyl monooxime	4	2,3-butanedione	57 <sup>c</sup>

a) The products obtained show satisfactory physical data and spectral data.

b) The product was purified through a short column of silica gel ( mesh size 60-120 ) using toluene-pet-ether as the eluent.

### Experimental section :

**Typical procedure of deoximation :** To the mixture of acetophenoneoxime (0.67g, 5 mmol), 15 ml toluene and 2g activated silchrom was added. The reaction mixture was stirred at 72-75<sup>o</sup> C for 2.5 hours. The reaction mixture was filtered through

sintered glass funnel and the residue was washed with 15 ml toluene. Excess toluene was removed by distillation and the residual acetophenone was recovered in 92 % yield.

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**Justification :**

1. We have reported here, for the first time the use of silica supported chromium trioxide reagent (silchrom) for deoximation under heterogeneous conditions.
2. Silchrom is much easier to prepare than other supported or unsupported chromium trioxide reagents, thus eliminating tedious solvent removal step.
3. Regeneration of aldehydes, ketones and 1,2- diketones from aldoximes, ketoximes and  $\alpha$ -oximinoketones respectively was greatly enhanced using silcrome.
4. Aldehyde oxime were deoximated in high yields.
5. Our deoximation method is very fast, simple, safe and general.

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