

Conversion of Oximes into Carbonyl Compounds with Glycinium Chlorochromate Supported Onto Silica Gel

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Glycinium chlorochromate supported onto acidic silica gel was reacted with oximes and converts them to their corresponding carbonyl compounds in good yields.

Key Words: Oxime, Carbonyl compounds, Glycinium chlorochromate.

INTRODUCTION

Since oximes have been employed as ketone or aldehyde functional group equivalents in organic synthesis¹, the conversion of oximes into their parent carbonyl compounds has received considerable attention. Oximes are useful protecting groups² and are extensively used for the purification and characterization of carbonyl compounds as well as in the preparation of amides³. Owing to the relative hydrolytic stability of oximes⁴, a wide variety of deoximation reagents have been developed such as manganese triacetate^{5a}, dinitrogen tetraoxide^{5b}, trimethylsilyl chlorochromate^{5c}, titanium silicalite^{5d}, pyridinium chlorochromate^{5e}, bismuth trichloride^{5f}, ammonium persulfate-silica gel^{5g}, sodium periodate^{5h}, zirconium sulfophenyl phosphonate⁵ⁱ, N-halo-amides^{5j}, triethylammonium chlorochromate^{5k} and Raney nickel^{5l}, with certain limitations. The use of dimethyl dioxirane⁶ was restricted to ketoximes whereas pyridinium chlorochromate-H₂O₂⁷ suffers from the disadvantage of over-oxidation. Deoximation using pyridinium chlorochromate^{5e} suffered from the serious drawback that the reaction time was too long and the poor yields.

In this communication, a new oxidative method for deoximation using a new reagent (glycinium chlorochromate (GCC) supported onto silica gel), as an oxidizing agent is reported. This method has been proved better oxidative method for deoximation than the other oxidative methods developed so far.

Deoxygenation with this reagent can occur in different condition like as reflux and microwave condition (Fig. 1).

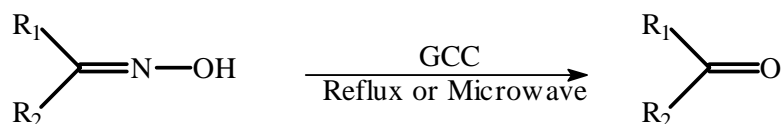


Fig. 1. Deoxygenation of oximes over silica gel confined GCC

EXPERIMENTAL

Procedure for preparation of glycinium chlorochromate: Chromium trioxide (2 g, 20 mmol) was added to a magnetically stirred solution of 6 N HCl (3.68 cc, 22 mmol) at a room temperature. The homogeneous solution was cooled to 5°C, Glycine (1.5 g, 20 mmol) was added over 20 min and stirred for 6 h at -6°C. A brown colour solution was obtained which was added to 8 g silica gel and dried under vacuum. This reagent must be used freshly.

General procedure for deoxygenation reaction under microwave irradiation: Mixture of GCC (2.98 mmol) supported onto silica gel and oxime (1 mmol) was ground with a pestle and irradiated in microwave oven for the time specified in Table-1.

The progress of reaction was monitored by TLC using petroleum ether:ethyl acetate (4:1). After completion of the reaction, the product was extracted with CH₂Cl₂ then the mixture was filtered off. The filtrate was evaporated to give the relative carbonyl compounds in very high yields.

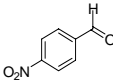
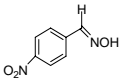




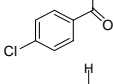
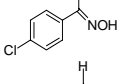

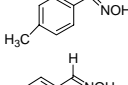





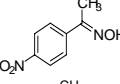
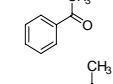
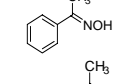


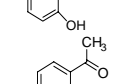
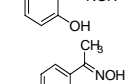



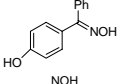



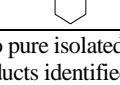




General procedure for deoxygenation reaction under reflux condition: Mixture of GCC (2.98 mmol) supported onto silica gel and oxime (1 mmol) was reflux in CH₂Cl₂ for the time specified in Table-1.

After completion of the reaction, the mixture was filtered off. The filtrate was evaporated to give the relative carbonyl compounds. The progress of reaction was monitored by TLC using petroleum ether:ethyl acetate (4:1).

RESULTS AND DISCUSSION

Using GCC supported onto silica gel on various oximes has been successfully deoxygenated to give corresponding carbonyl compounds and the results are summarized in Table-1. From obtained results, it was found that electron withdrawing groups on aromatic ring in comparison with electron releasing groups decreased the reaction times, which may be due to the steric effect of the electron withdrawing groups.

TABLE-1

m.p./b.p. ^c (°C)		Yield ^b (%)		Time ^a (min)		Product	Substrate	Entry
Lit ^d	Obs.	II	I	II	I			
106	108	99	98	10	2			1
58	58	96	94	12	3			2
44	46	97	93	13	2			3
47	46	99	97	14	3			4
204 ^e	203 ^e	96	87	15	3			5
38	39	96	92	20	4			6
197 ^e	195 ^e	90	89	60	5			7
248 ^e	246 ^e	88	89	35	3			8
78	77.5	98	95	50	3			9
200 ^e	200 ^e	99	95	120	4			10
226 ^e	224 ^e	98	98	140	4			11
218 ^e	217 ^e	95	89	150	5			12
106	104	91	88	155	5			13
51	51	99	99	120	4			14
135	133	93	91	150	5			15
155 ^e	155 ^e	98	92	60	3			16
165 ^e	165 ^e	98	97	90	3			17

^aI: is microwave condition, II: is reflux condition. ^b Yields refer to pure isolated products and were reported by GC (HP 19095 J-323, HP-5 column). ^c Products identified by their m.p./b.p., ¹HNMR and IR. ^d m.p. and b.p. was reported by Merck index. ^e Boiling point.

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