

Silica Gel Supported Collidinium Chlorochromate: A New Reagent for Selective Oxidation of Benzylic Alcohols

MOHAMMAD VAHDAT[†], MAHMOUD TAJBAKSH^{*}, ROBABEH BAHARFAR,
FARAJOLLAH MOHANAZADEH[‡] and LOTFI SHIRI[¶]

Department of Organic Chemistry, Mazandaran University, Babolsar, Iran
Fax: (98)(11)(25242002); E-mail: tajbaksh@umz.ac.ir; m_t_jadidi@yahoo.com

The new and mild chromium(VI) oxidant agent, collidinium (2,4,6-trimethylpyridinium) chlorochromate supported onto silica gel, was prepared as a stable yellow solid. The reagent is suitable for efficient and selective oxidation of benzylic alcohols to the corresponding carbonyl compounds in excellent yields.

Key Words: Oxidation, Benzylic alcohols, Carbonyl compounds, Collidinium chlorochromate.

INTRODUCTION

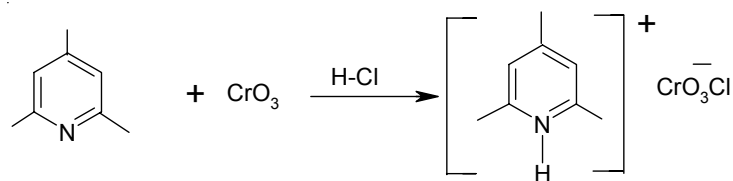
The oxidation of alcohols to aldehydes and ketones is one of the most important and frequently used functional group interconversion¹⁻³. Recently, attention has been paid to the preparation of new reagents suitable for such purposes⁴⁻⁷. The most important synthetic application of chromium oxidants is the oxidation of alcohols to carbonyl compounds⁸⁻¹⁰. Pyridium dichromate¹¹ and chlorochromate¹² have often been used for this purpose because of mild reaction condition and high yields. Pyridinium chlorochromate in dichloromethane¹² is a versatile oxidizing agent of high efficiency; however, work-up of the reaction mixture is tedious¹³. Chromium oxidants adsorbed on solid supports such as pyridinium chlorochromate on alumina¹³, chromic acid on silica^{14,15} and chromyl chloride on silica/alumina¹⁶ have been reported to give better yields under milder conditions than the corresponding parent oxidants. One significant difficulty associated with these reagents is the necessity of careful purification of the crude in order to remove chromium by-products from the desired carbonyl components. The oxidation of alcohols by montmorillonite K-10 supported *bis*(trimethylsilyl) chromate^{17,18} is also reported. In this communication, the authors reported collidinium chlorochromate supported on silica gel is a useful and selective oxidizing agent for benzyl alcohols.

[†]Department of Chemistry, Islamic Azad University, Ayatollah Amoli Branch, Iran.

[‡]Institute of Industrial Chemistry, Iranian Research Organization for Science and Technology, Tehran, Iran.

[¶]Elam University, Elam, Iran.

Collidinium chlorochromate can be easily prepared by addition of available collidine (2,4,6-trimethylpyridine) to an equivalent of chromic anhydride and hydrochloric acid at room temperature (**Scheme-I**). The resulting yellow crystalline complex is non-hygroscopic, air stable and is effective at least after 3 months of storage. The structure of the product was confirmed by elemental analysis and the IR spectrum exhibits peaks characteristic of the chromate ion. Collidinium chlorochromate supported on silica gel was then prepared by mixing equal weight of reagent with silica gel. When a variety of benzylic alcohols were treated with two equivalents of this supported reagent, the corresponding carbonyl compounds were obtained in high to excellent yields. Without silica gel, the reactions are sluggish and some benzyl alcohol is observed on TLC. This oxidation however is limited to benzylic alcohols and cinnamyl alcohol. No over oxidation to carboxylic acid was observed in the case of primary alcohols, even after prolonged heating with an excess of reagent. Cinnamyl alcohol was successfully oxidizing to the corresponding α,β -unsaturated aldehyde. In this case use of excess oxidant was avoided in order to prevent further oxidation. In this reaction, no trace of benzaldehyde could be detected.

**Scheme-I****EXPERIMENTAL**

All products are known compounds and characterized by comparison of their physical and spectroscopic data with those of authentic samples.

Preparation of collidinium chlorochromate: Chromium(VI) oxide (10 g, 0.11 mmol) was added with stirring and rather rapidly to 6 M hydrochloric acid (18.4 mL, 0.11 mol). After completion of dissolution of chromium(VI) oxide, to the mixture collidine (14.85 mL, 0.11 mol) was added under vigorous stirring. The resulting yellow slurry is stirred for further 1 h at room temperature. The solid was filtered off and washed with cold distilled water (2×15 mL). The yellow solid was dried in vacuo for 3 h to afford the title compound. Yield 18.0 g (70 %); m.p. 204-5 °C, elemental analysis: for $C_8H_{12}NO_3ClCr$ Calcd. (%) C (37.29), H (4.69), N (5.44); Found (%) C (37.10), H (4.50), N (5.20).

General procedure for oxidation of alcohols with silica gel supported collidinium chlorochromate: In a round-bottomed flask (100 mL)

equipped with a condenser and a magnetic stirrer, a solution of an appropriate alcohol (1 mmol) in CH_2Cl_2 (15 mL) was prepared. To this solution, collidinium chlorochromate (2 mmol), which was supported by equivalent weight of silica gel by mixing, was added. The resulting mixture was refluxed for indicated time. The progress of reaction was monitored by TLC (benzene/ethyl acetate 9:1). Upon the completion of reaction, the mixture was filtered off and washed with ether (3×20 mL). The filtrates were combined and evaporated to dryness. The crude was then directly subjected to column chromatography using hexane/ethyl acetate as eluent to afford the pure carbonyl compound (Table-1).

TABLE-1
OXIDATION OF BENZYLIC ALCOHOLS WITH
COLLIDINIUM CHLOROCHROMATE

Substrate	Product	Time (min)	Yield (%) ^a	m.p. or b.p. (°C)	
				Found	Reported ¹¹
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	$\text{C}_6\text{H}_5\text{CHO}$	15	80	178	178.1
<i>o</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OH}$	<i>o</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	25	80	211	211.9
<i>o</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	<i>o</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	85	60	44	43.5-4
<i>p</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OH}$	<i>p</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	10	65	213	213-4
<i>p</i> - $\text{BrC}_6\text{H}_4\text{CH}_2\text{OH}$	<i>p</i> - $\text{BrC}_6\text{H}_4\text{CHO}$	25	70	66	67
<i>p</i> - $\text{MeC}_6\text{H}_4\text{CH}_2\text{OH}$	<i>p</i> - $\text{MeC}_6\text{H}_4\text{CHO}$	15	90	204	204-5
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OH}$	<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	15	96	250	249.5
$\text{C}_6\text{H}_5\text{COCHOHC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$	65	70	95	95-6
$\text{C}_6\text{H}_5\text{CHOHC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	40	82	48	48
<i>p</i> - $\text{ClC}_6\text{H}_4\text{CHOHC}_6\text{H}_5$	<i>p</i> - $\text{ClC}_6\text{H}_4\text{CHOHC}_6\text{H}_5$	50	92	77	77-8
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CHOHCH}_3$	<i>p</i> - $\text{MeOC}_6\text{H}_4\text{COCH}_3$	35	75	39	38-9
$\text{C}_6\text{H}_5\text{CHOHCH}_3$	$\text{C}_6\text{H}_5\text{COCH}_3$	35	70	21	20.5
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	60	80	254	253

^aYields referred to isolated products.

RESULTS AND DISCUSSION

The concept of utilizing reagents absorbed on inert inorganic supports for organic reactions is well documented¹⁸⁻²⁷ and has been applied especially to chromium compounds^{18,20-23}. Since organic synthesis by solid phase methods is a powerful tool¹⁵ and chromium oxidants like pyridinium chlorochromate absorbed on alumina¹⁴, chromic acid on silica¹⁶ and chromyl chloride on silica-alumina have been reported to give better yields under mild conditions as compared to the parent oxidants. This reagent is easily prepared by adding silica gel to an aqueous solution of collidinium chlorochromate followed by evaporation to dryness on a rotary evaporator. The yellow-orange solid can be stored at room temperature and in light at

least for 3 months. The reaction is simply performed by stirring an excess of oxidant with alcohols in a solvent *e.g.*, dichloromethane. The product can be easily isolated by filtration and removal of solvent. Interestingly, this absorbed reagent is effective for benzylic alcohols (Table-1) and therefore can be used for selective oxidation of benzylic alcohols in the presence of other hydroxyl groups.

In summary, collidinium chlorochromate supported onto silica gel can be easily prepared and acts as an excellent reagent for oxidation of benzylic alcohols. The products can easily be separated by simple filtration of the solvent; therefore, no aqueous work up is needed.

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