

# Prolinium Chlorochromate as a New Mild and Efficient Oxidant for Alcohols

M. Mamaghani, F. Shirini, and F. Parsa

Chemical Department, Faculty of Science, Guilan University, Rasht, Iran

Received December 29, 2001

**Abstract**—Prolinium chlorochromate was prepared by an easy procedure and applied on a silica gel. The reagent was stable and was successfully used for conversion of benzyl and nonbenzyl alcohols into the corresponding carbonyl compounds under mild conditions and in high yield (90–98%).

A great interest is constantly attracted by organic reactions performed on the surface of solid carriers [1, 2], namely, on zeolites [3], clay [3], silica gel [1, 2, 4], alumina [1, 2, 5], and polymers [6, 7]. In the last decade a serious effort was made in development of new oxidants based on chromium(VI) on carriers for efficient and selective oxidation of organic substrates under mild conditions [8–11].

In extension of our studies on development of new reagents based on chromium(VI) on inert carriers we present here prolinium chlorochromate on silica gel (**I**) as a mild and efficient oxidant for alcohols. Reagent **I** is easily prepared from proline, chromium(VI) oxide, and 6 N HCl taken in molar ratio 1:1:1.1 (yield 94%), and then the prolinium chlorochromate is applied on silica gel by adding to a vigorously stirred silica gel suspension in water with subsequent evaporation to dryness on a rotary evaporator. The structure of the reagent was established from  $^1\text{H}$  NMR spectrum ( $\text{D}_2\text{O}$ ),  $\delta$ , ppm: 2.6 t (1H,  $J$  6 Hz), 1.9 t (2H,  $J$  6 Hz), 1.3 m (4H), and IR spectrum (KBr), where definite absorption bands were present at 1040, 950 and 760  $\text{cm}^{-1}$ , corresponding to the stretching vibration of the Cr=O bond in the anion  $\text{ClCrO}_3^-$ . These data are consistent with the previously observed bands for  $\text{ClCrO}_3^-$  in  $\text{KCrO}_3\text{Cl}$  and  $\text{BrCrO}_3^-$  in quinolinium bromochromate [12]. Reagent **I** is soluble in water, sparingly soluble in acetonitrile, and insoluble in dichloromethane, chloroform, benzene, and hexane. The pH value for 0.001 M water solution of prolinium chlorochromate is 3.3, and this value is higher than that of pyridinium

chlorochromate (1.75) and zinc chlorochromate monohydrate (2.3) [13, 14].

At the beginning of our study we tested the oxidative ability of prolinium chlorochromate without the carrier and on the carrier by the example of benzyl alcohol oxidation in boiling hexane (oxidant to substrate ratio was 3:1). It turned out, that the reagent on silica gel was more efficient oxidant for benzyl alcohol: The reaction took less time (1.33 h), whereas without carrier the process proceeded for 6 to ~90% conversion.

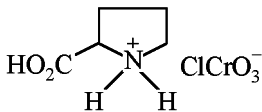
We believe that the reagent adsorbed on silica gel provides specific spatial arrangements increasing its reactivity.

Therefore we decided to carry out oxidation of benzyl alcohols using 3 equiv of the reagent on silica gel (at smaller amount of reagent the conversion was lower and the reaction time longer). The reaction was performed in boiling hexane and furnished the corresponding carbonyl compounds in excellent yields (90–98%) (see table). The oxidation of benzhydrol (run no. 6) and phenyl-substituted nonbenzyl aliphatic alcohols (run nos. 8, 9) required longer time and more reagent. Interestingly, the cinnamic alcohol (run no. 10) is more readily oxidized (20 min).

We conclude that prolinium chlorochromate on silica gel is an efficient reagent for oxidation of benzyl and nonbenzyl alcohols into the corresponding carbonyl compounds. We did not find any traces of products produced by further oxidation (carboxylic acids).

## EXPERIMENTAL

All reagents used in this study were purchased from Merk, Fluka, or Aldrich Companies. The



## Oxidation of alcohols with prolinium chlorochromate on silica gel

Run no.	Substrate	Products	Ratio oxidant : substrate	Time, h	Yield, <sup>a,b,c</sup> %
1	Benzyl alcohol	Benzaldehyde	3 : 1	1.33	98
2	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	3 : 1	0.75	97
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	3 : 1	1	90
4	2-Bromobenzyl alcohol	2-Bromobenzaldehyde	3 : 1	0.5	98
5	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	3 : 1	1.66	94
6	Benzhydrol	Benzophenone	3 : 1	4	91
7	1-Phenylethanol	1-Phenylethanal	3 : 1	1.66	95
8	3-Phenyl-1-propanol	3-Phenylpropanal	5 : 1	5.5	90
9	1-Phenyl-2-propanol	1-Phenyl-2-propanone	5 : 1	3	93
10	Cinnamic alcohol	Cinnamaldehyde	5 : 1	0.33	95

<sup>a</sup> Yield of isolated compound.

<sup>b</sup> All products were identified by comparison with authentic samples.

<sup>c</sup> In all experiments the reaction reached 100% conversion.

products were identified by comparison of their physical and spectral data with authentic samples. The melting points were measured on Electro Thermal device and were presented without correction. IR spectra were recorded on Shimadzu IR-470 instrument. <sup>1</sup>H NMR spectra were registered on spectrometer Bruker AC, FT-NMR (80 MHz) in CDCl<sub>3</sub>, external reference TMS. TLC was carried out on plates Merck Kieselgel 60H, F<sub>254</sub>, Art. no. 7730. The same grade silica gel was used as carrier for the reagent.

**Preparation of prolinium chlorochromate on silica gel carrier.** To 6 N HCl (9.2 ml, 0.055 mol) was added at stirring with a magnetic stirrer 5 g (0.05 mol) of chromium(VI) oxide. In 5 min a homogeneous solution formed that was cooled to 5°C, and to the solution within 10 min was added 5.75 g (0.05 mol) of proline. Then the mixture was stirred for 6 h at -6°C. The arising dark-brown solution was evaporated in a vacuum to obtain 11.8 g (0.047 mol) of prolinium chlorochromate as dark-brown solid (yield 94%). IR spectrum (KBr): 3200 v.s, 1690 s, 1600 v.s, 1440 s, 1040 w, 760 m cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (D<sub>2</sub>O): 2.6 t (1H, J 6 Hz), 1.9 t (2H, J 6 Hz), 1.3 m (4H) ppm.

Prolinium chlorochromate (1.25 g, 5 mmol) was added to silica gel (5 g) suspension in water (2.5 ml), and was stirred till uniform mixture formed. The solvent was evaporated in a vacuum at 40°C till the target reagent on the carrier was obtained.

**General procedure for benzyl alcohols oxidation.** To a solution of an alcohol (0.25 mmol) in hexane (4 ml) was added the reagent on carrier (0.75–1.25 mmol, see the table), and the mixture was stirred at reflux. The reaction progress was monitored by TLC (eluent CCl<sub>4</sub>-Et<sub>2</sub>O, 6:1), and the reaction was carried out till complete consumption of the initial alcohol. The final mixture was filtered, the precipitate was washed with hexane (3×5 ml), and the filtrate was evaporated on rotary evaporator to furnish the desired carbonyl compound. The structure of oxidation products was confirmed by comparison of their physical and spectral data with authentic samples.

We are grateful to the Scientific Council of Guilan University for the financial support of this study.

## REFERENCES

1. Laszlo, P., *Preparative Chemistry Using Supported Reagents*, Acad. Press: San Diego, 1987.
2. Smith, K., *Bull. Soc. Chim.*, 1988, p. 272.
3. Kabalka, G. and Pagni R., *Tetrahedron*, 1997, vol. 53, p. 7999.
4. Basiuk, V.A., *Russ. Chem. Rev.*, 1995, vol. 64, p. 1003.
5. Posner, G.H., *Angew. Chem. Int. Ed.*, 1978, vol. 17, p. 478.
6. Laszlo, P., *Acc. Chem. Res.*, 1986, vol. 19, p. 121.
7. Fruchtel, J.S. and Jung G., *Angew. Chem. Int. Ed.*,

- 1996, vol. 17, p. 35.
8. Shirini, F., Tajik H., and Jalili F., *Synth. Commun.*, 2001, vol. 31(19), p. 2885.
9. Heravi, M.M., Ajami, D., and Tabar-Hydar, K., *Monatsh. Chem.*, 1998, vol. 130, p. 1305.
10. Heravi, M.M., Ajami, D., and Tabar-Hydar, K., *Synth. Commun. Chem.*, 1999, vol. 29, p. 163.
11. Heravi, M.M., Ajami D., and Ghassemzaden M., *Synthesis*, 1999, p. 393.
12. Ozgun, B. and Degirmenbasi, N., *Synth. Commun.*, 1996, vol. 26(19), p. 3601.
13. Firouzabadi, H. and Sharifi, A., *Synthesis*, 1999, p. 999.
14. Tajbakhsh, M., Ghaemi, M., Sarabi, S., Ghassemzaden, M., and Heravi, M., *Monatsh. Chem.*, 2000, vol. 131, p. 1213.