Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Ammonium Chlorochromate Adsorbed on Silica Gel: A New Reagent for the Oxidation of Alcohols and Benzoins to Corresponding Carbonyl Compounds

Gui-Sheng Zhang [a] , Qi-Zeng Shi [a] , Mi-Feng Chen [a] & Kun Cai [a]
[a] Department of Chemistry , Henan Normal University , Xinxiang, 453002, P. R. China
Published online: 22 Aug 2006.

To cite this article: Gui-Sheng Zhang , Qi-Zeng Shi , Mi-Feng Chen & Kun Cai (1997) Ammonium Chlorochromate Adsorbed on Silica Gel: A New Reagent for the Oxidation of Alcohols and Benzoins to Corresponding Carbonyl Compounds, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:21, 3691-3696, DOI: 10.1080/00397919708007289

To link to this article: http://dx.doi.org/10.1080/00397919708007289

SYNTHETIC COMMUNICATIONS, 27(21), 3691-3696 (1997)

AMMONIUM CHLOROCHROMATE ADSORBED ON SILICA GEL: A NEW REAGENT FOR THE OXIDATION OF ALCOHOLS AND BENZOINS TO CORRESPONDING CARBONYL COMPOUNDS

Gui-Sheng Zhang*, Qi-Zeng Shi, Mi-Feng Chen, Kun Cai

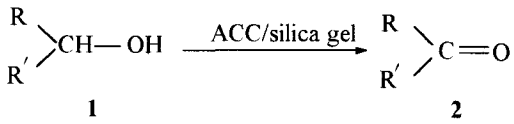
Department of Chemistry, Henan Normal University, Xinxiang 453002, P. R. China

ABSTRACT: A new reagent, Ammonium chlorochromate adsorbed on silica gel, suitable for the oxidation of alcohols and benzoins to the corresponding carbonyl compounds is described.

The concept of utilizing reagents adsorbed on inert inorganic supports for organic synthesis has been reported, and applied especially to chromium compounds[1~7]. These reagents oxidize a wide variety of alcohols to carbonyl compounds with the advantages of mild reaction condition, convenient isolation of the oxidized product and high yield but they have the disadvantage of being photosensitive and unstable. These reagents can be kept for only several weeks under vacuum in the dark before use.

* To whom correspondence should be addressed.

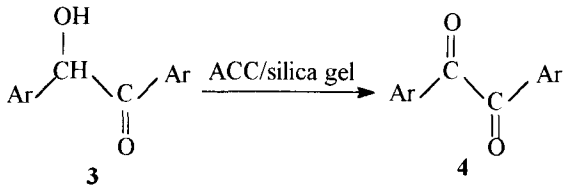
We have reported that ammonium chlorochromate adsorbed on alumina is a convenient oxidation for alcohols and benzoins to the corresponding carbonyl compounds[8]. In the same perspective we report now that ammonium chlorochromate adsorbed on silica gel (ACC/silica gel) is a new reagent suitable for oxidation of alcohols **1**, even with sensitive structure like allylic alcohols, to the corresponding carbonyl compounds **2** and of benzoins **3** to corresponding benzils **4** with the same advantages as other reagents described above. In addition, the present reagent is more stable than the above reagents ,it can be kept in for several months in air at room temperature without losing its activity.



1 **2**

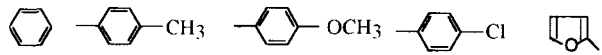
a R = C_6H_5, R′ = H b R = C_6H_5, R′ = CH_3
c R = C_6H_5CH=CH, R′ = H d R =  , R′ = H

e R = CH_2=CH, R′ = H f R = R′ = C_6H_5
g R , R′ = —$(CH_2)_5$— h R , R′ = —$(CH_2)_4$—
i R = $C_6H_5CH_2$, R′ = H j R = $CH_3(CH_2)_8$, R′ = H
k R = $CH_3(CH_2)_6$, R′ = H



3 **4**

Entry: a b c d e

Ar: 

This reagent is easily prepared by addition of a weighed amount of silica gel to a solution of ammonium chlorochromate in water and rotary evaporating to dryness. The adsorbed reagent is remarkably effective in oxidizing alcohols and benzoins to corresponding carbonyl compounds. The reaction is simply performed by stirring excess oxidant with alcohols or benzoins in cyclohexane at suitable temperature. The reaction product is then isolated by filtration of the reagent and removal of the solvent by distillation. The results obtained from the oxidation of 11 alcohols and 5 benzoins are reported in the **Table 1** and **Table 2**

Table 1 The oxidation of alcohols with ACC/silica gel

Alcohols (1)	Temp. (℃)	Time (h)	Ratio of oxidant/1	Yield [a,b] (%)	m.p. or b.p./kPa of 2	
					Found(℃)	Lit.[9](℃)
1a	30	2	2	95(91)	61/1.33	62/1.33
	60	1.5	2	94(89)		
1b	30	2	3	94(87)	83.5/1.60	83/1.60
	60	1	3	95(90)		
1c	30	3	2	91(80)	130/2.67	130/2.67
	60	2	2	92(81)		
1d	30	3	2	80(61)	68/2.67	68/2.67
	60	2	2	79(41)		
1e	30	2	2	75[c]		
1f	60	4	3	(80)	46.5 ~ 49	47~49
1g	60	3	3	90(83)	48/2.00	47/2.00
1h	60	3	3	89(85)	129/101.3	130/101.3
1i	60	3	2	70(65)	78/1,33	78/1.33
1j	60	3	2	85(80)	94.5/1.60	94/1.60
1k	60	3	2	86(81)	71/2.67	72/2.67

a Yields determined by G.L.C., unless otherwise noted

b Figures in parentheses are yields of isolated product. All compounds isolated had identical spectral characteristics with the corresponding authentic samples

c Determined by 2,4-D.N.P.

Table 2 The oxidation of benzoins with ACC/silica gel

Benzoins (**3**)	Temp. (℃)	Time (h)	Ratio of oxidant/**3**	Yield (%)	m.p.(℃) of **4** Found	Lit.
3a	60	14	2.5	95	94~96	92~94[10]
3b	60	16	2.5	91	101~104	103~104[10]
3c	58	14	2.5	90	132~134	130~133[10]
3d	56	15	2.5	79	195~197	195~196[11]
3e	55	16	2.5	85	162~164	164~165[12]

Experimental

Preparation of ACC /silica gel

To a solution of chromium trioxide (40g, 0.4mol) in water (100mL) is added ammonium chloride (21.4g, 0.4mol) within 15min at 40 ℃.The mixture is cooled until a yellow-orange solid forms. Reheating to 40 ℃ gives a solution .Silica gel (200g, 100~200 mesh) is then added to the solution with stirring at 40℃. After evaporation in a rotary evaporator, the orange solid is dried in vacuum for 2h at 70 ℃.The reagent can be kept for several months in air at room temperature without losing its activity.

Oxidation of Benzalcohol to Benzaldehyde; Typical Procedure

The above reagent (17g, 26mmol) is added to a flask containing a solution of benzalcohol (1.4g, 13 mmol) in cyclohexane (20mL). after stirring for 2h, the solid is filtered , washed with three 30 mL portion of ether. The combined filtrates are evaporated and vacuum distilled to afford benzaldehyde; yield: 1.25g (91%); b.p. 62 ℃/1.33kPa. **2b~2k** is obtained as the similar way . The results from the oxidation of **1a~1k** are summarized in the **Table 1**.

Oxidation of Benzoin to Benzil; Typical Procedure

To a solution of benzoin (1g, 4.7mmol) in cyclohexane (15mL) , the above reagent (7.65g, 11.7mmol) is added and the mixture is stirring for 14h at 60℃.The solid is filtered , washed several times with ether. The combined filtrates are evaporated and the residue is recrystallized from EtOH to get 0.94g of the product (**4a**) as a yellow needles; yield: 95%;m.p. 94~96℃; IR (KBr) ν_{max}: 1655 , 1590 , 1580 , 790 , 725 , 690 , 680 cm^{-1}; ^{1}HNMR ($CDCl_3$, 60 MHz) δ_H: 7.15~7.90 (m, Ar-H).

4b~4e are obtained in the same way; **4b**: IR (KBr) ν_{max}: 1655, 1590, 1565, 1450, 875, 835, 780, 740, 680 cm^{-1}; ^{1}HNMR ($CDCl_3$, 60 MHz) δ_H: 2.40 (6H, s, $2CH_3$), 7.30, 7.80 (8H, dd, J=8Hz, Ar-H). **4c**: IR (KBr) ν_{max}: 1660, 1600, 1510, 880, 830 cm^{-1}; ^{1}HNMR ($CDCl_3$, 60 MHz) δ_H: 3.80 (6H, s, $2CH_3$), 6.95, 7.80 (8H, dd, J=8Hz, Ar-H). **4d**: IR (KBr) ν_{max}: 1650, 1590, 880, 820, 730 cm^{-1}; ^{1}HNMR ($CDCl_3$, 60 MHz) δ_H: 7.41, 7.78 (8H, dd, J=8.7Hz, Ar-H). **4e**: IR (KBr) ν_{max}: 1650, 1400, 1290, 1030, 940, 810, 760 cm^{-1}; ^{1}HNMR ($CDCl_3$, 60 MHz) δ_H: 6.60 (2H, m) , 7.66 (4H, m). The results from the oxidation of **4a~4e** are summarized in the **Table 2**.

Acknowledgment

Project 29577273 Supported by National Natural Science Foundation of China.

References

1. Cheng ,Y. S., Liu, W. L., Chen ;S. H.. *Synthesis* **1980**, 223
2. Lou ,J.,D., Wu, Y. Y.. *Synth. Commun.* **1987**,17,1717
3. Lou ,J. D.. *Synth. Commun.* **1989**,19,1841

4. Filippo Jr, J. S., Chern, C. I.. *J. Org. Chem.* **1977**, 42, 2182

5. Lalancette ,J. M., Rollin ,G., Dumas, P. *Can. J. Chem.* **1972**, 50, 3058

6. Singh ,R. P., Subbarao, H. N., Dev, S. *Tetrahedron* **1979**, 35, 1789

7. Santaniello, E., Ponti, F., Manzocchi, A. *Synthesis* **1978**,534

8. Zhang G.S., Shi Q.Z.,Chen M.F.,Cai K.. *Synth. Commun.* **1997**, in press

9. Buckingham J. Donaghy S.M.."*Dictionary of Organic Compounds*". 5th ed. New York, **1982**

10. Ho, T. L. *Synthesis* **1972**,697

11. Gomberg, M., Van Natta, F. J. *J. Am. Chem. Soc.* **1929**, 51, 2241

12. Citterio, A. *Tetrahedron Lett.* **1978**,30,2701

(Received in the Netherlands 20 May 1997)