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

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ABSTRACT: A new reagent. ammonium chlorochromate adsorbed on alumina. 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 a disadvantage of photosensitive and unstable. these reagents should be kept for only several weeks under vacuum in the dark before use.

In the same perspective we report now that ammonium chlorochromate adsorbed on alumina 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.

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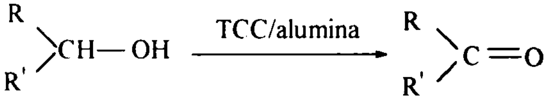


1 **2**

a R= C_6H_5, R'= H b R= C_6H_5, R'= H

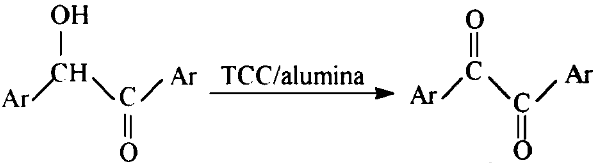
c R= C_6H_5CH=CH, R'= H d R=  , R'= H

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

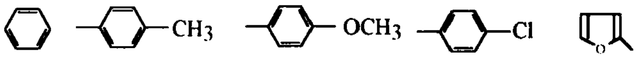
k R= $CH_3(CH_2)_6$, R'= H



3 **4**

Entry: a b c d e

Ar:



This reagent is easily prepared by addition of a weighed amount of alumina 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**.

Experimental

Preparation of Ammonium Chlorochromate /alumina

To a solution of chromium trioxide (20g, 0.2 mol) in water (50ml) is added ammonium chloride (10.7g, 0.2mol) within 15min at 40℃. The mixture is cooled until a yellow-orange solid forms. Reheating to 40℃ gives a solution. Alumina (120g, 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 50℃. 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 (15g. 19.5mmol) is added to a flask containing a solution of benzalcohol (1g. 9.75 mmol) in cyclohexane (20ml). after stirring for 1h, the solid is filtered . washed with three 20 ml portion of ether. The combined filtrates are evaporated and vacuum distilled to afford benzaldehyde; yield: 0.89g (91%);b.p. 62℃/1.33kPa.

Table 1 The oxidation of alcohols with ammonium chlorochromate

Alcohols (1)	Temp.(℃) /Time(h)	Ratio of oxidant/ 1	Yield [a,b] (%)	m.p. or b.p./kPa of 2	
				Found(℃)	Lit.[8](℃)
1a	30/1	2	96(91)	61/1.33	62/1.33
	60/0.6	2	97(90)		
1b	30/2	3	94(90)	83.5/1.60	83/1.60
	60/1	3	96(89)		
1c	30/3	2	90(81)	130/2.67	130/2.67
	60/2	2	90(80)		
1d	30/2	2	80(61)	68/2.67	68/2.67
	60/1.5	2	79(41)		
1e	30/2	2	80[c]		
1f	60/4	3	(86)	46.5~49	47~49
1g	60/3	3	96(90)	48/2.00	47/2.00
1h	60/3	3	95(86)	129/101.3	130/101.3
1i	60/3	2	70(65)	78/1.33	78/1.33
1j	60/3	2	86(81)	94.5/1.60	94/1.60
1k	60/3	2	85(80)	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.

Oxidation of Benzoin to Benzil; Typical Procedure

To a solution of benzoin (1g. 4.7mmol) in cyclohexane (15ml) . the above reagent (9g, 11.7mmol) is added and the mixture is stirring for 14h at 58℃.The solid is filtered . washed several times with ether. The combined filtrates are evaporated and the residue is recrystallized from EtOH to get 0.91g of the product (**4a**) as a yellow needles ; yield: 92% ; 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).

Table 2 The oxidation of benzoins with ammonium chlorochromate

Benzoins (3)	Temp.(℃)/ Time(h)	Ratio of oxidant/3	Yield (%)	m.p.(℃) of 4 Found	Lit.
3a	58/14	2.5	92	94~96	92~94 [9]
3b	60/16	2.5	90	101~104	103~104 [9]
3c	58/14	2.5	89	132~134	130~133 [9]
3d	56/15	2.5	90	195~197	195~196 [10]
3e	55/16	2.5	79	162~164	164~165 [11]

4b~**4e** are obtained in the same way: **4b**: IR (KBr) ν_{max}: 1655, 1590, 1565, 1450, 875, 830, 780, 740 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}: 1660, 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).

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