Pyridinium Chlorochromate Adsorbed on Alumina as a Selective Oxidant for Primary and Secondary Alcohols

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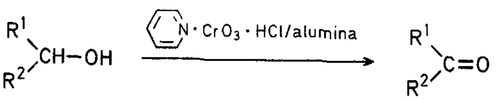
Pyridinium chlorochromate[1] [$CrO_3 \cdot C_5H_5N \cdot HCl$] oxidizes a wide variety of alcohols to carbonyl compounds in dichloromethane solution with high efficiency, but the difficulty still lies in the working up of reaction mixture.

The concept of utilizing reagents adsorbed on inert inorganic supports for organic reactions has recently been reported[2,3,4], and applied especially to chromium compounds[5,6,7,8]. We now report that pyridinium chlorochromate adsorbed on alumina is a suitable reagent for the oxidation of alcohols to aldehydes and ketones.



The adsorbed reagent provides a particular reaction environment capable of enhancing the reactivity of several reactants, the oxidation of carveol gives a 93% yield in 2 h,

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Table. Oxidation of Alcohols to Aldehydes and Ketones with Pyridinium Chlorochromate Absorbed on Alumina

Alcohol	Solvent/ time [h]	Ratio of oxidant/ alcohol	Yield[a,b] [%]	m.p. or b.p./torr of product	Lit. m.p. or b.p./torr	Oxidation by other methods	
						reagent	yield
carveol	n-C_6H_{14}/2	1.6	98 (93)	104 °C/11	88 °C/4[9]	pyridinium chlorochromate	82[18]
2-ethylhexanol	n-C_6H_{14}/2	2.5	97 (87)	65 °C/15	163 °C/760[10]		
furfuryl alcohol	C_6H_6/1.5	2.5	98 (45)	68 °C/20	90 °C/65[11]	CrO_3/pyridine complex	46[13]
menthol	n-C_6H_{14}/5	2.5	97 (94)	96 °C/20	116 °C/41[12]	CrO_3	94[12]
tetrahydrogeraniol	n-C_6H_{14}/2.5	2.5	95 (80)	87 °C/11			
citronellol	n-C_6H_{14}/4	3	97 (82)	90 °C/14	47 °C/1[13]	pyridinium chlorochromate	82[1]
β-methylallylalcohol	n-C_6H_{14}/0.2	3	98	69 °C/760	68.4 °C/760[10]		
2-methylcyclohexanol	n-C_6H_{14}/10	2.5	99 (83)	89 °C/20	104 °C/116[12]	CrO_3	80[12]
cinnamyl alcohol	C_6H_6/0.4	2	98 (84)	130 °C/20	129 °C/20[14]	CrO_3/pyridine complex	81[17]
isopulegol	n-C_6H_{14}/6	2.5	97 (81)	95 °C/14	100 °C/18[15]		
cholesterol	C_6H_6/2.5	3	97 (80)	122 °C	119.5–121 °C[16]	CrO_3/pyridine complex	64[16]

[a] Yield determined by G.L.C.

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

whereas use of pyridinium chlorochromate gives only 82% in 3 h (mol ratio 1:1.6). The mildly acidic character of pyridinium chlorochromate must be modified by buffering the reaction mixture[1] with powdered sodium acetate to avoid oxidation of citronellol to pulegone, but citronellol can be directly oxidized to citronellal with pyridinium chlorochromate adsorbed on alumina. The oxidation of cholesterol to the ketone is also satisfactory. Thus, 5-cholesten-3-one is produced in 80% yield (97% G.L.C. yield) by treatment of cholesterol with the oxidant in benzene at room temperature for 2.5 h (mol ratio 1:3). No 4-cholesten-3-one could be detected in the reaction product, but a small amount (2% G.L.C. yield) of cholest-4-ene-3,6-dione was obtained. Moreover, oxidation by pyridinium chlorochromate adsorbed on alumina turns out to be very profitable in the working up, which becomes reduced to a mere filtration. The reaction is very clean, and the isolation of products is simple.

The reagent is easily prepared by adding alumina to a solution of pyridinium chlorochromate and rotary evaporating to dryness. The yellow-orange solid is kept in vacuum at room temperature and stored in the dark before use. The average capacity of the dried reagent is 1 mmol/g of alumina. The alcohols are dissolved in n-hexane or benzene depending on the solubility.

The adsorbed reagent is remarkably effective in oxidizing primary and secondary alcohols to aldehydes and ketones, respectively, in high yields. The reaction is simply performed by stirring excess oxidant with alcohol in a suitable solvent at room 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 are reported in the Table and where possible compared with the results from other methods.

Pyridinium-Chlorochromate Absorbed on Alumina:
To a solution of chromium trioxide (6 g) in 6 normal hydrochloric acid (11 ml) is added pyridine (4.75 g) within 10 min at 40 °C. The mixture is kept at 10 °C until a yellow-orange solid forms. Reheating to 40 °C gives a solution. Alumina (50 g) is then added to the solution with stirring at 40 °C. After evaporation in a rotary evaporator, the orange solid is dried in vacuum for 2 h at room temperature. The reagent can be kept for several weeks under vacuum in the dark without losing its activity.

Oxidation of Carveol to Carvone; Typical Procedure:
The above reagent (7.5 g, 6.1 mmol) is added to a flask containing a solution of carveol (0.60 g, 3.8 mmol) in n-hexane (10 ml). After stirring for 2 h, the solid is filtered, washed with three 10 ml portions of ether. The combined filtrates are evaporated and vacuum distilled to afford carvone; yield: 0.54 g (93%); b.p. 104 °C/11 torr.

G.L.C., I.R., and N.M.R. analysis of the product thus obtained indicates a purity of 96% (G.L.C. conditions: 10% Carbowax 20M on 60–80 mesh Chromosorb W).

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