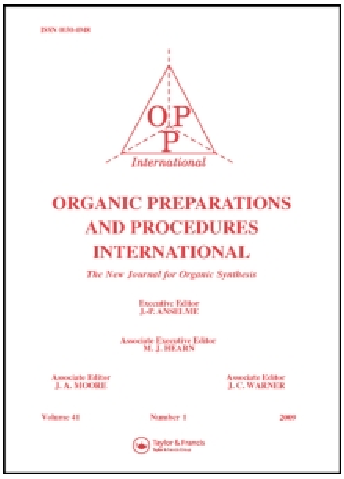

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PREPARATION OF ALUMINA-SUPPORTED DIMETHYLAMMONIUM CHLOROCHROMATE (DMCC) AND ITS USE IN THE OXIDATION OF ALCOHOLS AND BENZOINS

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4-(*p*-Chlorophenyl)-3,6-8-tricyano-2-hydroxy-5,7-diphenyl-1H-quinoline Hydrochloride (11).- A mixture of **7b** (0.01 mol, 4.49 g) and ammonium acetate (0.01 mol) in acetic acid (2 mL) was treated with ethyl cyanoacetate (0.01 mol, 1.13 g). The reaction mixture was refluxed for 3 h and allowed to cool at room temperature, then poured into ice-cold water, and 2-3 drops of conc. HCl was added. The solid was collected and recrystallized from a mixture of ethanol and dimethylformamide (1:1).

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PREPARATION OF ALUMINA-SUPPORTED DIMETHYLAMMONIUM CHLOROCHROMATE (DMCC) AND ITS USE IN THE OXIDATION OF ALCOHOLS AND BENZOINS

Submitted by
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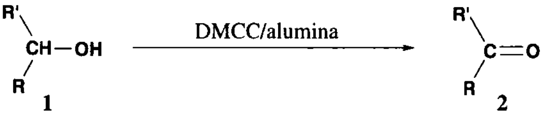
Chromium compounds have played an important role in the formulation of reagents adsorbed on inert inorganic supports as oxidants in organic synthesis.[1-7] These reagents oxidize a wide variety of alcohols to carbonyl compounds under mild reaction conditions and afford the products in high yields. However, they have the disadvantage of being photosensitive and unstable and can be stored for only several weeks under vacuum in the dark. We now report that dimethylammonium chlorochromate ($Me_2NH_2CrO_3Cl$, DMCC) adsorbed on alumina (DMCC/alumina) is a new reagent suitable for oxidation of alcohols, benzoins and also sensitive compounds such as allyl alcohol and cinnamic alcohol to the corresponding carbonyl compounds. In addition, DMCC/alumina is more stable than the above reagents[1-7] and may be kept for several months in air at room temperature without losing its activity. The reagent is not flammable and is stable at temperatures below 135°; it will change to a black solid slowly at temperatures above 135°. The reagent is easily prepared by the addition of alumina to a solution of dimethylammonium chlorochromate in water and followed by rotary evaporation to dryness. The reaction is performed by simple stirring of a mixture of the alcohol and the oxidant in cyclohexane at a suitable temperature. The product is isolated by filtration of the reagent and removal of the solvent by distillation. The results obtained from the oxidation of eleven alcohols and five benzoins are reported in Table 1. The oxidation of other functional groups with this reagent is under investigation.



a) R = Ph, R' = H b) R = Ph, R' = CH_3 c) R= PhCH=CH, R' = H d) R = 2-furyl, R' = H
e) R = CH_2=CH, R' = H f) R = R' = Ph g) R = R' = $-(CH_2)_5-$ h) R = R' = $-(CH_2)_4-$
i) R = $PhCH_2$, R' = H j) R = $CH_3(CH_2)_8$, R' = H k) R = $CH_3(CH_2)_6$, R' = H
l) R = Ph, R' = C_6H_5CO m) R = p-$CH_3C_6H_4$, R' = p-$CH_3C_6H_4CO$
n) R = p-$CH_3OC_6H_4$, R' = p-$CH_3OC_6H_4CO$ o) R = p-ClC_6H_4, R' = p-ClC_6H_4CO
p) R = 2-furyl, R' = 2-furoyl

EXPERIMENTAL SECTION

Mps were determined on a micro-melting point apparatus and are uncorrected. IR spectra were measured on a Nicolet FT-IR spectrometer. The ^1H NMR spectra were obtained on a Varian EM-360 A (60MHz) spectrometer in $CDCl_3$ with TMS as the internal standard.

Preparation of DMCC/Alumina.- To a solution of chromium trioxide (10g, 0.1mol) in water (10mL) was added dimethylamine hydrochloride (8.2g, 0.1mol) over 15min at 40°. The mixture was then cooled until a yellow-orange solid formed and was then reheated to 40° to give a solution. Alumina (60g, 100-200 mesh) was then added to the solution with stirring at 40°. After evaporation on a rotary evaporator at 60°, the orange solid was dried in vacuum at 50° for 1 h. The reagent may be kept for several months in air at room temperature without losing its activity.

Oxidation of Benzyl Alcohol to Benzaldehyde. Typical Procedure.- To a solution of benzyl alcohol (1.4g, 13 mmol) in cyclohexane (15mL) was added 20.3g (26mmol) of DMCC/alumina in one portion. After stirring for 2 h at 30°, the orange solid, which became deep brown, was then filtered and washed with ether. The combined filtrates were evaporated and the residue was distilled *in vacuo* to afford 1.25g (91%) of benzaldehyde, bp. 62°/10 mmHg. Compounds **2b-2k** were obtained in a similar fashion (Table 1).

Oxidation of Benzoin to Benzil. Typical Procedure.- To a solution of benzoin (1g, 4.7mmol) in cyclohexane (15mL), the reagent (7.4g, 9.4mmol) was added and the mixture was stirred for 12 h at

60°. The orange solid, which became deep brown, was then removed by filtration and washed several times with ether. The combined filtrates were evaporated and the residue was recrystallized from EtOH to yield 0.89g (90%) of the product **2l** as a yellow needles, mp. 94-96°. IR (KBr): 1655, 1590, 1580, 795, 720, 690, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): δ 7.15-7.90 (m, Ar-H).

Compounds 2m-2p were obtained in the same way; **2m**: IR (KBr):1655, 1590, 1565, 1450, 875, 835, 755, 730, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): δ 2.40 (6H, s, $2CH_3$), 7.28, 7.80 (8H, dd, J = 8Hz, Ar-H). **2n**: IR (KBr):1670, 1600, 1510, 880, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): δ 3.80 (6H, s, $2CH_3$), 6.90, 7.76 (8H, dd, J = 8Hz, Ar-H). **2o**: IR (KBr): 1650, 1590, 875, 820, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): δ 7.41, 7.72 (8H, dd, J = 8.7Hz, Ar-H). **2p**: IR (KBr): 1650, 1400, 1290, 1030, 940, 810, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): δ 6.60 (2H, m), 7.66 (4H, m).

TABLE 1. Oxidation of Alcohols with DMCC/alumina

Alcohols (1)	Temp. (°C)	Time (h)	Ratio of oxidant/1	Yield[a,b] (%)	mp. or bp./mmHg of **2** Found(°C)	lit.(°C)
1a	25-30	2	2	93(91)	61/10	62/10[8]
	55-60	1.5	2	94(89)		
1b	25-30	2	3	94(90)	83.5/12	83/12[8]
	55-60	1	3	96(89)		
1c	25-30	3	2	89(80)	130/20	130/20[8]
	55-60	2	2	87(78)		
1d	25-30	3	2	80(60)	68/20	68/20[8]
	55-60	2	2	70(40)		
1e	25-30	2	2	80[c]		
1f	55-60	4	3	(84)	46.5-49	47-49[8]
1g	55-60	3	3	90(86)	48/15	47/15[8]
1h	55-60	3	3	75(65)	129/760	130/760[8]
1I	55-60	3	2	89(60)	78/10	78/10[8]
1j	55-60	3	2	90(81)	94.5/12	94/12[8]
1k	55-60	3	2	86(80)	71/20	72/20[8]
1l	60	12	2	(90)	94-96	92-94[9]
1m	60	13	2	(82)	102-104	103-104[9]
1n	58	14	2	(78)	132-134	130-133[9]
1o	56	11	2	(85)	195-197	195-196[10]
1p	55	13	2	76)	162-164	164-165[11]

a) Yields determined by glc., 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 as 2,4-DNP

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A SIMPLE REGIOSELECTIVE NUCLEAR BROMINATION OF ALKYL PHENYL ETHERS

Submitted by (08/13/97)

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Oxohalogen acids and their organic and inorganic derivatives have been extensively employed as versatile, mild oxidizing and halogenating reagents in organic syntheses.[1] Sodium chlorite ($NaClO_2$, **1**) has enjoyed an important position in carbohydrate chemistry[2] and is also known as a specific reagent for the oxidation of aldehydes to carboxylic acids.[3] However, there has been no synthetically useful reactions other than the above oxidations. Indeed, reaction of aromatic hydrocarbons and of alcohols with aqueous $NaClO_2$ gave complex mixtures of products ascribed to the competing oxidation and chlorination.[4] Our recent investigation into *cleaner* syntheses using *in situ*