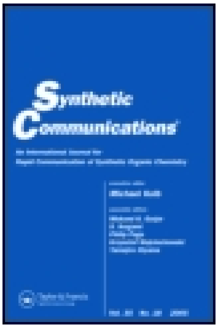

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Oxidation with Magnesium Chlorochromate

Per H. J. Carlsen [a] & Kari Aasb⊘ [a]

[a] Department of Chemistry University of Trondheim, The Norwegian Institute of Technology, N-70334, Trondheim, Norway

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OXIDATION WITH MAGNESIUM CHLOROCHROMATE.

Per H.J. Carlsen* and Kari Aasbø

Department of Chemistry
University of Trondheim,
The Norwegian Institute of Technology
N-70334-Trondheim, Norway

Abstract. Magnesium chlorochromate, **MCC**, oxidizes secondary alcohols to ketones in good yields. Primary alcohols gave aldehydes in low to moderate yields only, together with rearranged products.

Chromium reagents are among the most commonly used oxidation agents in organic chemistry. Chlorochromates came into prominence in 1975 by the introduction of pyridinium chlorochromate[1]. Since then a host of analoges and their properties as oxidation agents have appeared in the literature, amoung them potassium chlorochromate[2]. In the search of new selective and inexpensive chlorochromate salts, we have investigated the magnesium salt, $Mg(CrClO_3)_2$, **MCC**.

MCC was easily prepared by the reaction of magnesium chloride with chromium trioxide in aqueous solution in accordance with a known procedure[3]. However, this salt was formed with 9 molecules of crystal water. As the water may affect the properties of the reagent, the anhydrous salt was also desired for the study. Removal of crystal water was attemped by standard dehydration methods, but

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* To whom correspondence should be addressed.

resulted in the formation of intractable materials only. We have therefore devised an alternative procedure for the preparation of anhydrous **MCC**. Powdered anhydrous magnesium chloride and chromium trioxode were reacted in carbon tetrachloride at room temperature. This gave a red powder. The IR spectrum of this product was very similar to that of other chlorochromates. An X-ray analysis of the product indicated low crystallinity, and reflexes due to magnesium chloride and CrO_3 were not observed. This indicated that a reaction probably had taken place. While the evidence is not conclusive, we assumed that the product is the desired anhydrous **MCC** based on the IR and X-ray results.

Solubility. The **MCC** reagent exhibited good solubility in polar organic solvents, *e.g.*, acetonitrile, acetone and ethyl acetate, but was insoluble in chlorinated solvents, *e.g.*, dichloromethane and carbon tetrachloride, as well as in hexane, benzene and toluene. Solutions of anhydrous **MCC** were generally unstable and this reagent also reacted violently with DMSO and DMF. The hydrated salt, **MCC.H_2O**, was also easily soluble in the latter solvents. In general the solutions decomposed upon standing.

Oxidation of alcohols.

A series of alcohols were oxidized with **MCC.H_2O** and with the anhydrous magnesium reagent, **MCC**, in a CH_3CN-CH_2Cl_2 mixtures at room temperature. The molar ratio between alcohol and **MCC** was usually 1 : 1. In general both reagents reacted readily with secondary alcohols forming the ketones in good yields, table 1. The hydrated reagent, **MCC.H_2O** gave slighty higher yields.

Primary alcohols as a rule gave complex mixtures and the desired carbonyl products in low yields only, Table 2. Thus, 1-hexanol with both reagents, gave low yields of mixtures composed of hexanal,

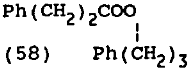
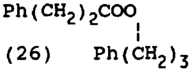
Table 1. Oxidation of secondary alcohols with **MCC** or **MCC.H_2O**

Substrate	**time h**	**Rea-gent**	**Product (%)**	**Yield % a)**
4-*tert*-Butyl-cyclohexan	0.5	MCC	4-*tert*-Butyl-cyclohexanone (100)	100
Fenchyl alcohol	3	MCC	Fenchone (100)	78
Dihydrocarveol	30	MCC	Dihydrocarvone (95)	56
Isopulegol	17	MCC	Isopulegone (90)	60
1-Phenylethanol	15	MCC	Acetophenone (100)	78
	15	MCC.H_2O	Acetophenone (100)	91

a) Isolated yield. Yields were not optimized.

hexanoic acid and hexyl hexanoate. The ester formation appeared to be favored when using the anhydrous reagent. Over-all yields were generally higher when using the hydrated reagent. Faster conversion and higher yields were observed for reactions in dilute solution (0.1 M). Acid sensitive substrates may be affected by the acidity of the reagents. Thus, citronellol upon reaction with **MCC** yielded citronellal together with the *ene*-product isopulegone. Linalool gave low yields of citral together with cyclization product 2,2,6-trimethyl-6-vinyl-tetra-hydropyran-3-one. Cinnamyl alcohol gave low to moderate isolated yields of mixtures of cinnamaldehyde and benzaldehyde.

Table 2. Oxidation of primary alcohols with **MCC** and **MCC.H_2O**.

Substrate	**Time h**	**Reagent**	**Product (%)**	**Yield % a)**
Benzyl alcohol	2	MCC	Benzaldehyde (100)	60
	15	MCC. H_2O	Benzaldehyde (90) Benzoic acid (9)	96
3-Phenyl-propanol	72	MCC	3-Phenylpropanal (19)  $Ph(CH_2)_2COO-(CH_2)_3Ph$ (58)	9
	15	MCC. H_2O	3-Phenylpropanal (66)  $Ph(CH_2)_2COO-(CH_2)_3Ph$ (26) 3-Phenylpropiomic acid (4)	45
1-Hexanol	36	MCC	Hexanal (13) Hexanoic acid (8) Hexyl hexanoate (73)	13
	15	MCC. H_2O	Hexanal (34) Hexanoic acid (31) Hexyl hexanoate (30)	23
Citronellol	72	MCC b)	Citronellal (3) Isopulegone (81)	17
Linalool	72	MCC	Citral (7) 2,2,6-trimethyl-6-vinyl-tetrahydropuran-3-one (40)	24
Cinnamyl alcohol	17	MCC	Cinnamaldehyde (40) Benzaldehyde (56)	50
	15	MCC. H_2O	Cinnamaldehyde (59) Benzaldehyde (31)	64

a) Isolated yields. Yields were not optimized.
b) Ratio substrate : MCC = 1 : 2.5

Experimental.

Magnesium chlorochromate, MCC. Powdered anhydrous magnesium chloride (64.5 g, 0.68 mol) and chromium trioxide (135 g, 1.36 mol) in 700 ml of dry carbon tetrachloride were stirred vigorously for 3 days under a nitrogen atmosphere. The resulting deep red product was collected by filtration or by evaporating the solvent under reduced pressure. The yield was 197 g, 99 %. *IR (KBr):* 961, 945, 910, 612, 447 cm^{-1}.

Magnesium chlorochromate, hydrated, MCC.H_2O. was prepared by the method described in ref. 3. *IR (KBr):* 963, 945, 910, 607, 447 cm^{-1}

Oxidation of alcohols with MCC and MCC.H_2O, General procedure. The alcohol (10 mmol) was dissolved in 65 ml of a mixture of dichloromethane and acetonitrile under a nitrogen atmosphere. The ratio of dichloromethane : acetonitrile was set at 10 : 1 for **MCC.H_2O** and 4 : 1 for the anhydrous **MCC**. To this solution was added 10 mmol of the **MCC**-reagent. The resulting mixture was stirred for the time indicated in the tables. Then more dichloromethane (60 ml) was added together with 5 g of silica gel and the precipitate was removed by filtration. The solution was then filtered through a short silica column, which was washed with ether (50 ml) and acetone (50 ml). The combined organic solutions were concentrated under reduced pressure, and the product was worked up by crystallization or distillation

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