

Oxidation of Alcohols to Carbonyl Compounds Using Chromic Anhydride-Chlorotrimethylsilane-Alumina

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The oxidation of alcohols constitutes the synthetically most important application of chromium oxidation¹⁻². Aqueous acidic solutions of chromium(VI) compounds in the presence of co-solvents like acetic acid or acetone have been widely used. For the oxidation of alcohols to both aliphatic and aromatic aldehydes and ketones, chromium complexes and salts of heteroaromatic bases in nonaqueous solvents proved to be preferable owing to the mild reaction conditions and easy workup procedure². Recently, Aizpurua and Palomo³ reported that sodium dichromate or chromic anhydride-chlorotrimethylsilane in acetonitrile or dichloromethane is an efficient system for converting alcohols to the corresponding carbonyl compounds. This reagent system, however, totally fails to produce aldehydes from the reaction with primary aliphatic alcohols.

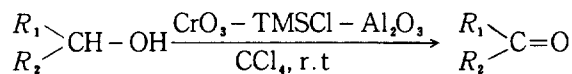
We now report that the addition of basic alumina to this oxidizing system remarkably improves the yield and selectivity for the oxidation of alcohols in general. The oxidation of 1-hexanol to hexanal is typical. Chromic anhydride (10 g, 100 mmol) and chlorotrimethylsilane (21g, 200mmol) were added to carbon tetrachloride (150 ml). The mixture was stirred for 30 minutes or until a dark red solution was obtained. Alumina (50g, 500mmol) was added. To the stirred heterogeneous solution was slowly added 1-hexanol (7.6g, 75 mmol) as a solution in a small amount of carbon tetrachloride. After 2 hours of vigorous stirring, the whole reaction mixture was filtered through a short column of silica gel. The clear filtrate was concentrated on a rotary evaporator. Distillation of the crude product using a short-path distilling apparatus or a Kugelrohr afforded 6.8g (83%) of pure hexanal (bp

Table 1. Oxidation of Alcohols to Aldehydes and Ketones with Chromic Anhydride-Chlorotrimethylsilane-Alumina

Aldehydes and Ketones	Alumina	Reaction Time(hr)	Yield(%) ^a	(mp.) or bp. °C	
				Found	Reported ¹⁰
hexanal	basic	2.0	83	131	131
	neutral	2.0	0 ^b		
	acidic	2.0	0 ^b		
	none	2.0	0 ^b		
octanal	basic	2.0	84	169-171	81/32
	acidic	2.0	0 ^b		
cyclohexanecarboxaldehyde	basic	2.5	80	161-163	159.3
	neutral	2.5	0 ^b		
	acidic	2.5	0 ^b		
	none	2.5	0 ^b		
benzaldehyde	basic	0.5	90	178-184	179/75
	acidic	0.5	83		
<i>p</i> -methoxybenzaldehyde	basic	1.0	94	127-130/12	113
	acidic	1.0	91		
<i>p</i> -nitrobenzaldehyde	basic	1.0	88	(105-108)	(106)
	acidic	1.5	83		
acetophenone	basic	1.5	93	53-56	56
	acidic	1.5	94		
2-methylcyclohexanone	basic	1.5	90	162-163	165-16
	acidic	1.5	86		
2-octanone	basic	1.0	94	171-173	173.6
	acidic	1.5	90		
2-hexanone	basic	0.5	93	122-124	127
	acidic	1.0	90		
cinnamaldehyde	basic	1.0	78 ^c	119-122/9	130/20
	acidic	1.0	47 ^c		

^aPurity of >98% was demonstrated by GC. ^bNo carbonyl compound was isolated. The recovery of starting alcohol was very low. ^c10-50% of benzaldehyde was also obtained.

129–131 °C). This oxidation can be carried out on a 1–30g scale without any problems or major modification of the procedure. The yields and reaction conditions for the oxidation of other alcohols are summarized in Table 1.



This new reagent system is superior or comparable in yields to any other popular chromium(VI) oxidizing agents such as PDC⁴, PCC⁵ and chromyl chloride adsorbed on silica-alumina.⁶ The reagent can be prepared from the cheap and easily accessible chemicals in less than an hour. The procedure is simple and straightforward.

The true oxidizing species generated from chromic anhydride and chlorotrimethylsilane is believed to be chromyl chloride or polyoxochromium(VI) dichloride rather than trimethylsilyl chlorochromate as Aizpurua and Palomo³ have postulated. The proton nmr spectrum of this reagent system shows only two kind of protons characteristic of chlorotrimethylsilane and hexamethyldisiloxane. It showed close resemblance to chromyl chloride in its reactions with olefins⁷ and arylmethanes⁸.

Chromyl chloride is known to be too vigorous to be used for the oxidation of alcohols, but silica-alumina chemi-adsorbed chromyl chloride was proved efficient for the oxidation of all kinds of primary and secondary alcohols to aldehydes and ketones⁶. Both acidic and basic alumina were proved to be effective for moderating the reactivity of chromic anhydride chlorotrimethylsilane pair, but the oxidation is very sluggish in the presence of neutral alumina. The oxidation of primary alcohols to aldehydes was successful only with basic alumina. By keeping the reaction mixture basic,

further oxidation to the acid or chlorotrimethylsilane-catalyzed acetal formation from unreacted alcohol and the product aldehyde seems to be greatly retarded. Addition of pyridine or sodium carbonate to keep the reaction media basic, however, did not improved the yield of carbonyl compounds.

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Medium-spin ($S = 3/2$) Ferric Complex of $\text{Fe}^{3+}\text{Mo}^{6+}\text{O}_4\text{Cl}\cdot(\text{C}_{14}\text{H}_{29}\text{NH}_2)_{1.7}$ as a Two-Dimensional Heisenberg Antiferromagnet

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The magnetic behavior of ferric ion is simple in general. They exhibit either high-spin ($t_{2g}^3e_g^2$) or low-spin ($t_{2g}^5e_g^0$) states with $S = 5/2$ and $1/2$, respectively. Only a few cases of molecular compound containing Fe^{3+} are known as a medium-spin ($t_{2g}^4e_g^1$) state with $S = 3/2$. The spin state of the complex is determined by the balance between the ligand field strength and the magnitude of exchange energy. Deviations from the normal spin states (high- and low-spin) can take place for ferric ions when the ligand field strength is of the same order as the mean pairing energy for the d^5 configuration. Recently we have, for the first time, prepared this kind of polymeric ferric complexes, $\text{FeMoO}_4\text{Cl}\cdot(\text{C}_n\text{H}_{2n+1}\text{NH}_2)_{1.7}$, in which the medium-spin state with ($t_{2g}^4e_g^1$) electronic configuration is stabilized.

FeMoO_4Cl is a layer type compound of which the synthesis, structure and some physical properties have been already reported in the previous papers.¹⁻⁴ Intercalation complexes of FeMoO_4Cl with n -alkylamines also have been reported for the first time with its EPR, IR and XRD results.¹ From XRD investigation, it has been verified that the intercalated n -alkylamines are arranged as paraffin-like bimolecular layers between the basal planes of the FeMoO_4Cl matrix. And as already shown in the idealized model of n -alkylamine complex, the pseudooctahedral FeO_4Cl_2 unit with D_{4h} symmetry in FeMoO_4Cl is degraded into the square pyramidal FeO_4Cl one with C_{4v} symmetry by the intercalation of n -alkylamines.¹

$\text{FeMoO}_4\text{Cl}\cdot(\text{C}_{14}\text{H}_{29}\text{NH}_2)_{1.7}$ is prepared by direct thermal