Oxidation of Some Primary and Secondary Alcohols Using Pyridinium Chlorochromate

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Abstract:

Pyridinium chlorochromate (PCC) (DCM) was used as a solvent . DCM is the solvent predominately used in such oxidations .The structures of the produced aldehydes and ketones were confirmed has been prepared and supported on activated carbon (charcoal). The oxidizing agent (PCC/charcoal) was used to prepare series of carbonyl compounds in a completion to the former published results. Dichloromethane in the light of spectral analysis (UV,IR,^{1}H-NMR) as well as some physical properties.

Key words : Oxidation of alcohols ,Corey-Suggs reagent , Pyridinium chloro chromate.

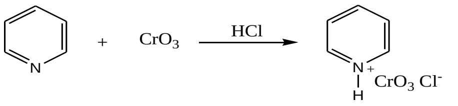
Introduction

Organic chemists must often choose from hundreds of oxidizing agents and reaction conditions to perform a desired oxidation without affecting other functional groups present or causing side reactions . Oxidation of primary alcohols to aldehydes without further oxidation to carboxylic acids is difficult to accomplish with oxidizing agents in aqueous solution because small amounts of aldehyde hydrates , which are in equilibrium with the aldehyde , are readily oxidized to the corresponding carboxylic acids.

$$RCH_2OH \xrightarrow{[O]} RCHO \xrightleftharpoons{H_2O} RCH(OH)_2 \xrightarrow{[O]} RCO_2H$$

However , selective oxidation of primary alcohols to aldehydes can be easily accomplished by using chromium (VI) reagents that are soluble in organic solvents under anhydrous conditions such as dichloromethane which avoids hydrate formation and , thus the oxidation of primary alcohols stops at the stage of an aldehyde .

The convenient reagent for this conversion is pyridinium chloro chromate ($C_5H_5NH^+CrO_3Cl^-$) which is often abbreviated as PCC and also known as Corey-Suggs reagent$^{(1)}$.



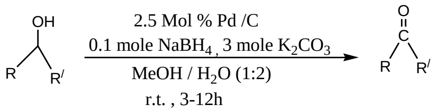
PCC is a readily available stable reagent , oxidizes a wide varity of alcohols to carbonyl compounds , also it is used as an oxidant for amino acids , aldehydes , L-cystine and aniline, deuterated alcohols, cycloalkanols, vicinal and non-vicinal diols and homo benzylic alcohols$^{(2)}$.

PCC is also remarkable for its high selectivity, for example , when oxidizing tertiary ally alcohols, unsaturated aldehydes are observed as the sole product.

This reaction is known as the Babler oxidation , otherwise such oxidations commonly afford dienes as by-products resulting from dehydration .

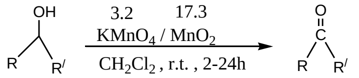
Another rotable oxidative reaction of PCC is its efficient conversion of unsaturated alcohols or aldehydes to cyclohexanones. This particular pathway is known as oxidative cationic cyclization$^{(3)}$.

While the use of Pd/C in aqeous alcohol with molecular oxygen, sodium borohydride, and potassium carbonate efficiently oxidation remarkable reactivation of active sites of the Pd surface$^{(4)}$.



R:Ar , vinyl
R$^/$:H , alkyl

Permanganate supported on active manganese dioxide can be used effectively for the oxidation of arenes$^{(5)}$.



R:alkyl , Ar
R$^/$:H , alkyl

Experimentral

All chemicals was supplied from Fluka , Sigma and Aldrich company .

Boiling points were determined by using paraffine oil.

U.V visible spectra were recorded using Shimadzu UV-Vissible spectrophotometer 160 (Department of Chemistry - College of Science - University of Mosul) .

Fourier-Transform Infrared spectra were recorded on Brucker Tensor spectrophotometer. 2003 (Germany) (Department of Chemistry - College of Science - University of Mosul) Nuclear magnetic resonance (^{1}H-NMR) spectra were registered at 300MHz Brucker spectrometer by using tetramethylsilane (TMS) as an internal standard, and $CDCl_3$ as solvent in Al-Bayt University in Jordan .

Prepartion of pyridinium chlorochromate$^{(6)}$ (PCC)

General procedure

To (3.819) ml of 6M HCL (0.11) mole was added to (9.99) gm (0.1) mole of CrO_3 rapidly with stirring , after (5) min the homogeneous solution was cooled to (0) ^{0}c and (8.08) ml (0.1) mole of pyridine was carefully added over (10) min . Recooling for (0) ^{0}c gave a yellow – orange solid which was collected by filteration and dried in room temperature for (48) hr,m.p (196-200^0) , yield (39.77%) .

Supporting PCC/ Charcoal$^{(7)}$

A (3) gm of activated charcoal was added with continueous stirring to about (6) gm of PCC in CH_2Cl_2 as a solvent. The resulting black solid (reagent on support) was filtered and dried under room temperature .

Oxidation of alcohols (General Procedure)(8)

In a (20) ml CH_2Cl_2 a (0.015) mole of PCC / charcoal was suspended, an alcohol (0.04) mole in DCM (2) ml was then added in one portion to the magnetically stirred suspension. After several hours (Table1) the resulting mixture was left for a while and then washed with dry ether and filtered. The solvent then removed by distillation (or by evaporation at r.t.), to get the corresponding carbonyl compounds : ketones or aldehydes.

Table -1- Names and some physical properties of (12-22)

Comp. No.	Alcohols	Comp. No.	Products	Reaction Time (hrs)	b.p (^0C)		Yield (%)
					Calc.	(Lit.)(9)	
1	Propane -1,2-diol	12	2-Oxopropanal	5	127-130	……..	19.42
2	2-Methyl cyclohexanol	13	2-Methyl cyclohexanone	24	167-169	166	28.35
3	Ally alcohol	14	Propenal	10	56	53	27.97
4	2-Butene -1,4-diol	15	Fumaraldehyde	24	143-145	……..	10.72
5	N-Methyl –p-piperidinol	16	N-Methyl -4-piperidone	5	65	55-60	33.63
6	Isobutyl alcohol	17	2-Methyl popionaldehyde	24	60	64	13.88
7	Amyl alcohol	18	Pentanal	10	110	104	18.34
8	Isoamyl alcohol	19	3-Methyl butanal	10	97	93	13.97
9	4-Methyl-2-pentanol	20	4-Methyl -2-pentanone	24	115-118	119	13.03
10	2-Methoxy ethanol	21	2-Methoxy ethanal	24	100	92	42.56
11	2-Ethyl hexanol	22	2-Ethyl hexanal	24	169	163	37.54

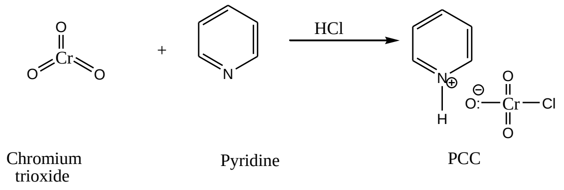
Results and Discussion

The structures of final aldehydes and ketones (12-22) were known and supported by the spectral data (UV , IR , ^{1}H-NMR) as well as some physical properties (see Tables 1-2) Compared with authentic samples . (figures 1 and 2)

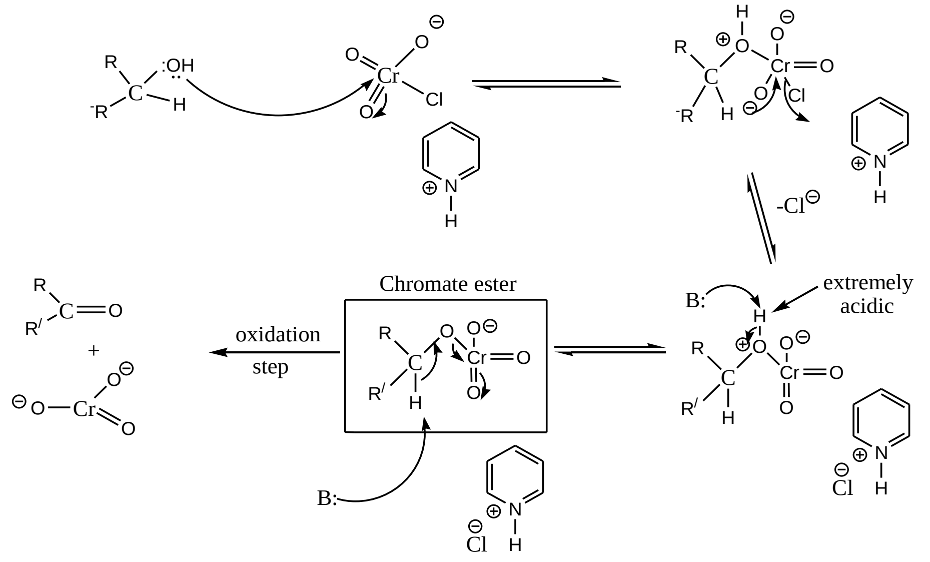
The quantities of PCC needed for normal oxidations (primary and secondary alcohols) are in the range of (2-5) g.

From the oxidation results of the studied alcohols we conclude that the oxidation times were relatively long compared to simple alcohols .

From the pathway for preparing PCC, it is found that the oxidizing component is the chlorochromate anion , $ClCrO_3^-$ (10) .

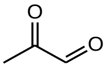


According to the spectral data were showed on Table (2) the studied mechanism for the reaction of PCC with primary and secondary alcohols can proposed by the two steps(11) :

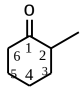


Mechanism for the oxidation of alcohols with PCC

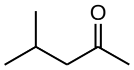
Table -2- spectral data (UV , IR , ^{1}H-NMR) of compounds (12 – 22)



(12)



(13)



(20)

Comp. No.	UV ($CHCl_3$) λ_{max} (nm)	IR(NaCl cell) for liquid ν (cm^{-1})		^{1}H-NMR ($CDCl_3$) δ ppm					
		C=O	C-H						
12	268	1720	....	CH_3 (d,3H,1.1)					
13	266	1705	....	CH_3 d,3H 0.95	C_5 P,2H 1.2	C_4 P,2H 1.7	C_3 q,2H 1.9	C_6 t,2H 2.2	C_2 h,1H 3
14	260	1723	2727 ,2864						
15	256	1710	2877						
16	260	1660	....						
17	296	1689	2729 ,2871						
18	302	1719	2873						
19	292	1719	2872						
20	288	1709	2722 ,2871	6H 2s 0.9	3H s 1.2	1H m 1.4	2H m 1.8		
21	260	1724	2733						
22	258	1707	2873						

The spectral analyses of all products: (UV, IR) and the ^{1}H-NMR results for some of the products (12 , 13 and 20) are shown on (Table 2) .

The compound 13 is chosen as a representative model for the spectral discussion .

The ^{1}H-NMR spectrum(12) showed a doublet signal at δ 0.95 ppm related to 3H of CH_3 whereas the pentent signal at δ 1.2 ppm is due to the 2H at C_5 . The 2H at C_4 seemed as another pentet signal at δ 1.7 ppm , but the quartet signal at δ 1.9 ppm attributed to 2H at C_3 . The triplet signal shown at δ 2.2 ppm corresponds to 2H at C_6 , Finally a hextet signal of 1H at C_2 seemed at δ 3.0 ppm .

The IR spectrum(13) showed a frequency of 1705 cm^{-1} related to the stretching vibration of the carbonyl group (Table 2) .

The UV spectrum(14) reflects a wavelength at maximum absorption of 266 nm compared with (302) nm of the measured spectra of starting material that related to the electronic transition ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) respectively (Table 2) .

The rest of the products were illustrated on Table -2- for their spectral data .

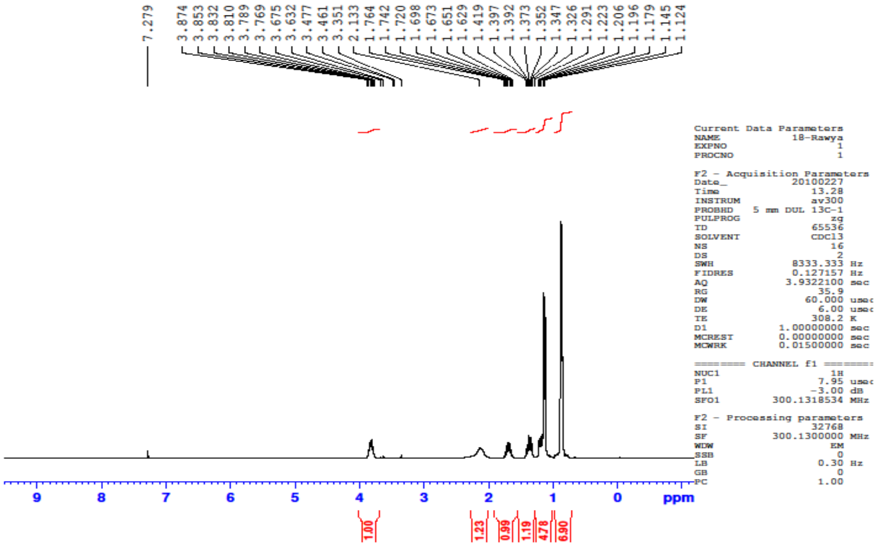


Figure (1) ^{1}H- NMR Spectrum of Compound (20)

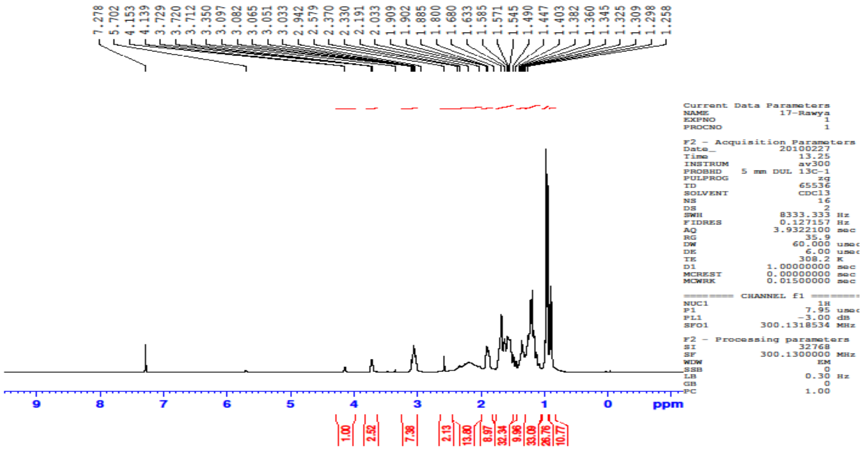


Figure (2) ^{1}H- NMR Spectrum of Compound (13)

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اكسدة بعض الكحولات الاولية والثانوية باستخدام كلوروكرومات البيريدينيوم

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الملخص

تم تحميل مادة كلورو كرومات البريدينيوم (PCC) على الفحم المنشط (charcoal) بعد تحضيرها واستعملت المادة المؤكسدة (PCC/ charcoal) لتحضير سلسلة من مركبات الكاربونيل استكمالا للمجاميع المنشورة في الادبيات ، واستعمل ثنائي كلوروميثان (DCM) وهو المذيب الاكثر شيوعا في عمليات الاكسدة من هذا النوع . وتم دعم تكون الكيتونات او الالديهايدات في ضوء الطرق الطيفية (UV ، IR ، ^{1}H-NMR) ، اضافة الى بعض الصفات الفيزياوية