

Quinolinium Chlorochromate: A New Reagent for Conversion of Primary and Secondary Alcohols to Carbonyl Compounds

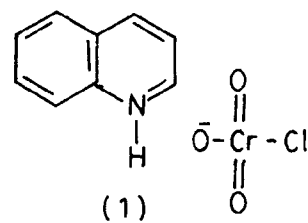
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Summary: The oxidation of a variety of primary and secondary alcohols including ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, 1-heptanol, cyclopentanol, cyclohexanol, benzyl alcohol, 2-chlorobenzyl alcohol, 1-phenyl-1-ethanol, 1-phenyl-1-propanol and furfuryl alcohol with quinolinium chlorochromate has been studied. As a result of oxidation, each primary alcohol yielded an aldehyde and each secondary alcohol yielded a ketone in reasonable yields. The reagent appears to be more effective for oxidation of aromatic and alicyclic alcohols as compared to oxidation of aliphatic alcohols.

Introduction

Due to a variety of causes the oxidation of primary and secondary alcohols to carbonyl compounds (aldehydes and ketones) has always remained a subject of special interest. Since aldehydes are easily oxidized to the corresponding carboxylic acids, the conversion of primary alcohols to the respective aldehydes requires the use of relatively mild oxidizing agents. Some of the oxidants that have commonly been used for this purpose include potassium dichromate [1], lead tetraacetate [2,3], N-bromosuccinimide [4], potassium permanganate [5], dimethylsulphoxide [6], aluminium tert-butoxide [7], chromium trioxide in glacial acetic acid [8], chromium trioxide in a mixture of sulphuric acid and acetone [9], chromium trioxide-pyridine complex [10,11], silver picolinate [12] and chromyl chloride [13]. Each of these reagents has its own limitations and drawbacks. Recently, pyridinium chlorochromate has also emerged [14,15] as a useful reagent for oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. Not only can pyridinium chlorochromate be easily prepared from chromium trioxide, pyridine and hydrochloric acid but it is also a stable compound and can be conveniently employed for oxidation of alcohols to the carbonyl compounds in almost neutral conditions. This usefulness of pyridinium chlorochromate tempted us to prepare quinolinium chlorochromate (1) and employ the newly prepared compound as an oxidant for conversion of primary and secondary alcohols to the corresponding carbonyl compounds. In this article we wish to report and discuss the results of these studies.



Results and Discussion

Quinolinium chlorochromate is a new oxidizing agent and is being reported for the first time. The reagent was successfully prepared from quinoline in the same manner as reported for preparation of pyridinium chlorochromate from pyridine. However, it may be emphasized that the isolation of the former was found to be more convenient than that reported for the later. For example, for the precipitation of pyridinium chlorochromate it is essentially required to cool the reaction mixture to 0°C whereas for the precipitation of quinolinium chlorochromate from the reaction mixture this is not essential. In fact it was found possible to isolate quinolinium chlorochromate in excellent yields in the temperature range of 0-22°C. It is also important to emphasize that the % yield of quinolinium chlorochromate, in several attempts, was always found to be higher (at least 92%) than the maximum yield reported for pyridinium chlorochromate (81%). In general the preparation of quinolinium chlorochromate appeared to be simpler and more convenient than that of pyridinium chlorochromate.

In the present studies fourteen primary and secondary alcohols were subjected to oxidation with quinolinium chlorochromate in *n*-hexane solvent. The primary alcohol substrates studied were ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-heptanol, benzyl alcohol, 2-chlorobenzyl alcohol and furfuryl alcohol. The secondary alcohols subjected to oxidation were 2-propanol, 2-butanol, cyclopentanol, cyclohexanol, 1-phenyl-1-ethanol and 1-phenyl-1-propanol. By using this reagent for oxidation, each alcohol substrate was successfully oxidized either to an aldehyde in case of a primary alcohol) or to a ketone in case of a secondary alcohol). The reaction conditions, the carbonyl products of oxidation and their % yields obtained by oxidation of alcohols are reported in Table 1. A comparison of the % yields of various carbonyl products reveals that the yields of the respective carbonyl compounds are generally lower for oxidation of aliphatic than those for the aromatic and alicyclic alcohols e.g. whereas oxidation of benzyl alcohol yield 88.5% benzaldehyde within two hours reaction time, hexanal is obtained in a yield of 42.0% by oxidation of 1-hexanol requiring six hours. Within the aliphatic series, the oxidation reaction appears to be more facile for lower aliphatic alcohols than for higher aliphatic alcohols e.g. ethanol yielded acetaldehyde in 60.4% yield at room temperature in three hours, 1-butanol yielded butanol in 52.1% yield after three hours of reflux and 1-heptanol yielded heptanal in 40.0% yield after six hours reflux. The two alicyclic alcohols, cyclopentanol and cyclohexanol also underwent oxidation to yield the respective ketones in relatively good yields.

Comparison with other method

The preparation of aldehydes and ketones by oxidation of the corresponding alcohols by some previously reported methods encounters certain limitations. It is well known that chromic acid oxidation [17] may give good yields but involves strongly acidic conditions thus formation of esters often reduces the yields of the carbonyl products. On the other hand, Oppenauer oxidation conditions are strongly basic and are conducive to condensation and polymerization reactions of the carbonyl products [18]. N-halocompounds used for oxidation of alcohols suffer from the disadvantage of being effective for benzylic alcohols only [4]. The oxidation of alcohols with quinolinium

Table 1: Oxidation of alcohols with quinolinium chlorochromate

Alcohol substrate	Reaction conditions	Carbonyl product	% Yield
Ethanol	Room temperature, 3h	Acetaldehyde	60.4
1-Propanol	Room temperature, 3h	Propionaldehyde	55.3
2-Propanol	Reflux, 3h	Acetone	59.2
1-Butanol	Reflux, 3h	Butanal	52.1
2-Butanol	Reflux, 3h	2-Butanone	56.3
1-Hexanol	Reflux, 6h	Hexanal	42.0
1-Heptanol	Reflux, 6h	Heptanal	40.0
Cyclopentanol	Reflux, 3h	Cyclopentanone	61.6
Cyclohexanol	Reflux, 3h	Cyclohexanone	58.3
Benzyl alcohol	Reflux, 2h	Benzaldehyde	88.5
2-Chlorobenzyl alcohol	Reflux, 3h	2-Chlorobenzaldehyde	58.5
1-Phenyl-1-ethanol	Reflux, 3h	Acetophenone	74.2
1-Phenyl-1-propanol	Reflux, 3h	Propiophenone	68.6
Furfuryl alcohol	Reflux, 3h	Furfural	59.6

*Room temperature: 15-17°, **The reaction started at room temperature but slowed down after 15 min.

chlorochromate does not suffer from such drawbacks and limitations. The reagent itself is quite stable and can be conveniently prepared in excellent yields. The oxidation procedure is relatively very simple and rapid. Furthermore, this method of oxidation can be applied to all types of alcohols in almost neutral conditions thus avoiding accompanying side reaction when the reaction conditions are either acidic or basic.

Experimental

Reagents and substrates

Ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, benzyl alcohol, diethyl ether, *n*-hexane, furfuryl alcohol and quinoline were supplied by E. Merck, 1-hexanol, cyclohexanol, 1-heptanol, cyclopentanol, 2-chlorobenzyl alcohol and hydrochloric acid were obtained from BDH. 1-phenyl-1-ethanol and 1-phenyl-1-propanol were Fluka chemicals. Chromium trioxide was supplied by May and Baker. All the commercially supplied chemicals were used without further purification.

The method applied for preparation of quinolinium chlorochromate from quinoline was essentially similar to that reported [14] for preparation of pyridinium chloroformate from pyridine. However, several attempts were made to improve

the reaction conditions and the yields of the products. The following method was found to be most satisfactory.

Into a 1-1 beaker containing hydrochloric acid (6 M, 184 ml) was added chromium trioxide (100 g, 1 mole) rapidly. The mixture was thoroughly stirred for five minutes and the resulting homogeneous solution was cooled to 15°. To this mixture quinoline (129.6 g, 1 mole) was added dropwise over a period of half an hour. After the addition of quinoline was over, the mixture was again cooled to 15°. This resulted in precipitation of quinolinium chlorochromate in the form of a yellow powder. The powder was filtered off and dried under vacuum for three hours, m.p. 239°, 93% yield.

Oxidation of alcohols

For oxidation of alcohols with quinolinium chlorochromate the procedure applied was similar to that reported [14] for oxidation of alcohols with pyridinium chloromate. To a mixture of quinolinium chlorochromate (0.08 mole) and n-hexane (150 ml) contained in a three necked 500-ml round bottomed flask fitted with a reflux condenser, was added the required alcohol (0.12 mole) in n-hexane (20 ml). In the case of ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, benzyl alcohol and furfuryl alcohol a brisk reaction was indicated by the rise in temperature of the reaction mixture. In all other cases the reaction had to be in-

itiated by warming the reaction mixture. The exact reaction conditions required for oxidation of various alcohols are given in Table 1. In the cases of oxidation of ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol, the carbonyl products were distilled off directly from the reaction flask. In other cases, after the reflux period was over the reaction mixture was filtered, the black gummy residue washed with diethyl ether (2 x 30 ml) and the washings mixed with the filtrate. From this ethereal solution ether was removed by evaporation and the residual liquid was treated with aqueous hydrochloric acid (6M, 50 ml) in order to remove free quinoline liberated during the oxidation reaction. The aqueous mixture was then extracted with diethyl ether (3 x 10 ml). The ethereal extract was subjected to removal of ether by evaporation. The residual crude liquid, in each case, when subjected to distillation yielded the corresponding carbonyl compound in pure form. The oxidation products and their % yields are also included in Table 1.

Characterization of the carbonyl products

The purity of each carbonyl product was established by comparative TLC against the authentic sample. The characterization of the isolated products was based on comparison of their observed boiling points with the values reported in the literature and the preparation of 2,4-dinitrophenylhydrazones and semicarbazone. The data concerning these aspects is given in Table 2. Furthermore, the IR spectrum (neat) of each carbonyl product

Table 2: Characterization of the isolated carbonyl compounds

Carbonyl product	Boiling point		2,4-Dinitrophenyl hydrazone M.P.		Semicarbazone M.P.	
	(Obs) ^o C	(Lit) ^o C	(Obs) ^o C	(Lit) ^o C	(Obs) ^o C	(Lit) ^o C
Acetaldehyde	231-22	21 ^a	149-150	147 ^a	161-162	162 ^a
Propionaldehyde	47-49	49 ^a	153-154	155 ^a	88-89	89 ^a
Acetone	55-56	56 ^b	127-128	126 ^a	188-189	190 ^a
Butanal	74-75	74 ^a	125-126	126 ^a	105	106 ^a
Butanone	79-81	80 ^b	115-116	115 ^b	145-146	146 ^b
Benzaldehyde	178-180	179 ^c	236-237	237 ^c	221-222	222 ^c
Hexanal	129-131	131 ^a	105-106	107 ^a	108-109	109 ^a
Heptanal	155-157	156 ^a	108-109	108 ^a	107-108	109 ^a
Cyclopentanone	130-132	131 ^b	147-148	147 ^b	207-208	209 ^b
Cyclohexanone	156-157	156 ^b	160-161	162 ^b	165-166	166 ^b
2-Chlorobenzaldehyde	212-213	213 ^c	205-206	207 ^c	225-226	225 ^c
Acetophenone	200-202	202 ^d	249-250	250 ^d	196-197	198 ^d
Propiophenone	216-218	218 ^d	192-193	191 ^d	180-181	181 ^d
Fufural	159-161	161 ^a	227-229	229 ^a	201-202	202 ^a

a-d refer to reference 19^a to 19^d respectively.

was recorded which displayed a strong C=O stretching peak [16] in the range varying from 1670 cm^{-1} to 1720 cm^{-1} depending upon the nature of the carbonyl product. In the case of aldehydes, the aldehydic C-H stretching peak [16] was also observed in the range of 2690-2760 cm^{-1} .

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