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Der Pharma Chemica, 2012, 4(4):1674-1678
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chlorochromate (BCC) as oxidizing agent

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ABSTRACT

Selected alcohols and oximes undergo oxidative cleavage to corresponding carbonyls by employing BCC, in chloroform as solvent under reflux conditions. It is found that this reagent also shows similar selectivity and mechanism for the oxidation of alcohols and oximes as PCC (pyridinium chlorochromate), MCC (1-methyl imidazolium chlorochromate), ICC (imidozolium chlorochromate) and QFC (quinolium fluorochromate).

Key words: Oxidation, alchohols, oximes, BMTC

INTRODUCTION

The search for mild, versatile, selective reagents for the operationally simple oxidation of alcohols and oximes to carbonyl compounds has long been the objective of many research laboratories. A variety of oxidizing agents containing the chromium (VI) ion have been studied [1] for this purpose, and the most important among them are the pyridinium chlorochromate [2] (PCC), imidazolium chlorochromate [3] (ICC), 1-methylimidazolium chlorochromate [4] (ICC), quinoline chlorochromate [5-8] and quinolium fluorochromate [9-10] (QFC), but a large number of them cannot be conveniently used in the modern organic synthesis, especially for the oxidation or preparation of complex or highly sensitive substances. Earlier, we have reported the utilization of 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (BMTC) as a mild oxidizing agent for the cleavage of N,N'-dimethyl hydrazones to carbonyl compounds [11] and as a catalyst in the preparation of 1,4-diketone [12-17]. We now report the formation and utility of 3-benzyl-5-(2-hydroxyethyl)-4-methyl 1,3-thiazolium chlorochromate (BCC) as an oxidizing agent.

MATERIALS AND METHODS

All the reagents and solvents are from Spectrochem and Aldrich and they were used as received without further purification. All reactions were carried out in an atmosphere of nitrogen. Chemical and solvents used were purchased either from Fluka or Merck. All the reagents were of analytical grade. Thin-layer chromatography (TLC) was performed on E.Merck AL silica gel 60 F254 plates and visualized under UV light. The IR spectra were recorded on a Perkin Elmer FT-IR spectrometer. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian EM-360 spectrometer (400MHz). The ^{13}C NMR spectra recorded in $CDCl_3$ on a Varian EM-360 spectrometer operating at 100MHz. All the chemical shifts were reported in δ (ppm) using TMS as an internal standard. The mass spectra were recorded on Agilent ion trap MS.

General procedure for the oxidation of alcohols and oximes

To a stirred suspension of BCC (0.15 mole) in chloroform (200 mL) in a 500 mL round bottom flask fitted with a reflux condensor, a solution of alcohol / oxime (0.1 mole) in chloroform (20 mL) was added and the reaction mixture was refluxed for the period indicated in **Table 1**. The course of the reaction was monitered by GC analysis / TLC (silica gel, petroleum ether – ethyl acetate, 9:1).

As soon as the reaction was complete, the reaction mixture was diluted with dry diethyl ether (200 mL), filtered through a short plug of silica gel and washed with diethyl ether (3 x 50 mL). The combined filterates on evaporation gave the crude product which was purified by distillation under reduced pressure or recrystallised from suitable solvent in the case of solid products.

Table I - Oxidation of alcohols and oximes with BCC

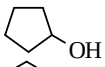
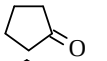
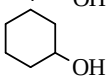
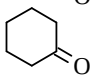
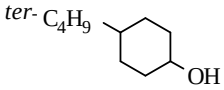
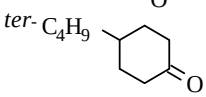
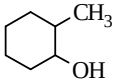
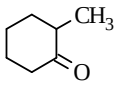
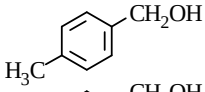
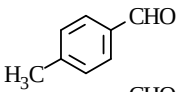
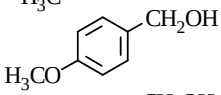
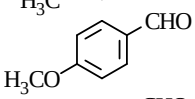
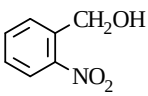
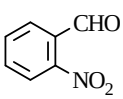
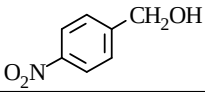
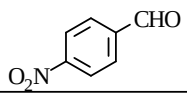
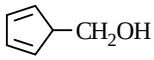
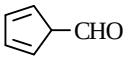
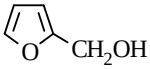
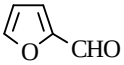
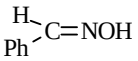
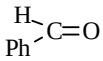
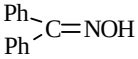
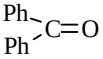
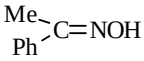
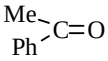
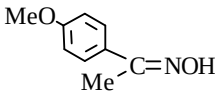
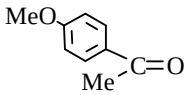
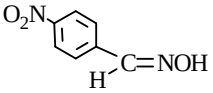
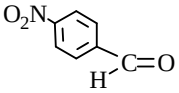
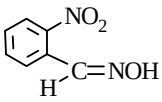
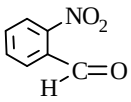
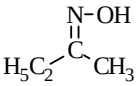
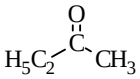
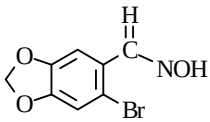
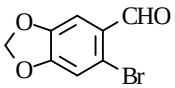
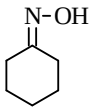
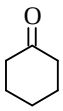
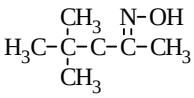
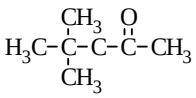
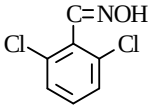
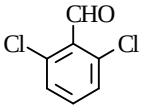
Entry	Substrate	Product	Substrate / Oxidant mole ratio	Time (hr)	Yield (%)
1	$n\text{-}C_4H_9\text{-}OH$	$n\text{-}C_3H_7\text{-}CHO$	1 : 1.5	3.0	75
2	$n\text{-}C_6H_{13}\text{-}OH$	$n\text{-}C_5H_{11}\text{-}CHO$	1 : 1.5	2.5	71
3	$n\text{-}C_5H_{11}\text{-}OH$	$n\text{-}C_4H_9\text{-}CHO$	1 : 1.5	5.0	79
4	$n\text{-}C_8H_{12}\text{-}OH$	$n\text{-}C_7H_{10}\text{-}CHO$	1 : 1.5	2.5	85
5	$n\text{-}C_{10}H_{21}\text{-}OH$	$n\text{-}C_9H_{19}\text{-}CHO$	1 : 1.5	6.0	90
6	$n = C_4H_9, C_2H_5CH\text{-}CH_2OH$	$n = C_4H_9, C_2H_5CH\text{-}CHO$	1 : 1.5	6.5	87
7	$C_6H_5, H_3C CH\text{-}CH_2OH$	$C_6H_5, H_3C C{=}O$	1 : 1.5	7.0	96
8	$n = C_6H_{13}, H_3C CH\text{-}CH_2OH$	$n = C_6H_{13}, H_3C C{=}O$	1 : 1.5	6.0	76
9	$C_3H_7, H_5C_2 CH\text{-}CH_2OH$	$C_3H_7, H_5C_2 C{=}O$	1 : 2.0	7.5	86
10			1 : 2.0	6.0	79
11			1 : 2.0	6.5	85
12			1 : 2.0	7.0	90
13			1 : 2.0	5.5	95
14	$Ph, Ph CH\text{-}OH$	$Ph, Ph C{=}O$	1 : 2.0	3.5	92
15			1 : 2.0	4.0	89
16			1 : 2.0	4.5	87
17			1 : 2.0	5.0	79
18			1 : 2.0	4.5	83

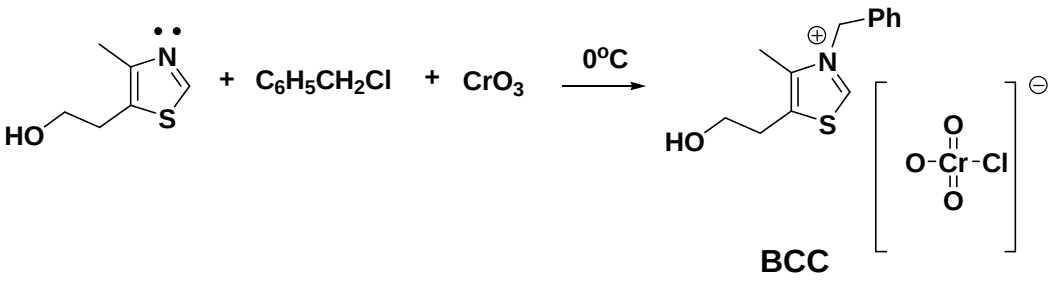
Table I Contd.,

Table I contd.,

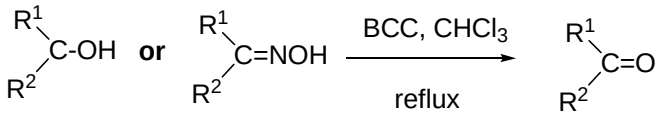
Entry	Substrate	Product	Substrate / Oxidant mole ratio	Time (hr)	Yield (%)
19			1 : 2.0	3.0	95
20			1 : 1.5	6.0	80
21			1 : 2.0	4.0	60
22			1 : 2.0	3.5	58
23			1 : 2.0	4.0	92
24			1 : 2.0	3.5	88
25			1 : 2.0	4.0	87
26			1 : 2.0	4.5	80
27			1 : 2.0	3.5	85
28			1 : 2.0	3.0	88
29			1 : 2.0	4.5	86
30			1 : 2.0	5.0	84
31			1 : 2.0	3.5	96

RESULTS AND DISCUSSION

3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chlorochromate was prepared by the rapid addition of CrO_3 (10 g, 1 mole) to benzylchloride (18.4 mL, 1.1 mole). After 10 min the homogeneous solution was cooled to 0°C and 3-benzyl-5-(2-hydroxy ethyl)-4-methylthiazole (7.9 gm, 1 mol) was carefully added over 10 min. Recooling to 0°C gave a yellow-orange solid which was collected on a sintered glass filter and dried in vacuum for 1 hr yield 8.5 g (88%) (**Scheme 1**),



Scheme 1-Preparation of BCC



R^1 = Alkyl, Aryl
R2 = H, Alkyl, Aryl

Scheme- 2 Oxidation of alcohols and oximes to corresponding carbonyl compounds

In this article we wish to report the selective oxidation of certain aliphatic and aromatic alcohols and oxidative deoximation of aromatic aldoximes and ketoximes to the corresponding carbonyl compounds brought about by BCC using chloroform as a solvent under reflux conditions (**Scheme 2**). The results of the oxidations reactions are summarized in **Table 1**. All the spectral data and physical properties of isolated carbonyl compounds are in agreement with the literature data.

In summary, this new method for the oxidation of alcohols and oximes to carbonyl compounds has some practical merits over previously reported methods, such as easy preparation of reagents, has a good stability and selectivity. Over the other reagents BCC has broad applicability for the oxidation of alcohols and oximes with sensitive functional groups. The present method of oxidation of selected alcohols and oximes using BCC is thus an efficient mild oxidizing agent and is an inexpensive method.

CONCLUSION

In conclusion we have demonstrated very efficient and practical method for the synthesis of carbonyl compounds by employing BCC as oxidizing agent (alcohols and oximes undergo oxidative cleavage to corresponding carbonyls). The simple experimental procedure is inexpensive and readily available catalyst with high yield of product is great advantages of present protocol.

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