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Oxidation of alcohols with zirconium dichromate tetra hydrate (ZDTH) to their corresponding carbonyl compounds in solution and under solvent free conditions

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ABSTRACT

Primary and Secondary benzylic and sturated alcohols are oxidized to their corresponding carbonyl compounds in good to high yields with zirconium dichromate tetrahydrate (ZDCTH) in dichloromethane or under solvent free conditions at room temperature.

KEYWORDS

Benzylic alcohols;
Carbonyl compounds;
Zirconium dichromate tetrahydrate (ZDCTH);
Neat conditions;
Oxidation.

INTRODUCTION

Oxidations with sodium or potassium dichromate as the source of chromium (VI) are usually Performed under aqueous acidic conditions. Sometiomes cosolvents like acetone, benzene, methylene chloride, or ether are used in order to solubilize water in soluble organic compounds. Under the conditions mentioned, the reagents oxidize almost every oxidizable functional groups ranging from carbon – hydrogen bonds to aromatic nuclei. Howere, the low PH of the reaction medium in the presence of water enhances hydrolytic reactions which restricts the use of this class of reagents for acid sensitive molecules[1].

Zirconium hydroxide chromate[2-4] and also organosilicon derivatives of chlorochromate are of interest and trimethylsilyl chlorochromate is prepared and reported as efficient oxidant[5]. We have found that zirconium cation activates oxoanions and make them useful for the oxidation of organic substrates in aprotic organic solvents.

In recent years, attention has been paid to reactions which are performed under neat conditions[6,7]. Therefore, the idea and the reports promoted us investigate the oxidation abilities of zirconium dichromate tetrahydrate (ZDCTH) for the oxidation of varieties of organic substrates under solvent free conditions at and secondary benzylic alcohols to their corresponding carbonyl compounds with high rates and yields under solvent free conditions.

Overoxidation of the aldehydes to carboxylic acids has not been observed in these reactions. In comparison with those reactions in solution the reactions under solvent free conditions are proceeded very fast, with lower molar ratios of the oxidants (TABLE 1).

We have found that oxidation of saturated alcohols needs harsh reaction conditions, which are oxidized to their corresponding carbonyl compounds with ZDCTH

TABLE 1 : Oxidation of alcohols with ZDCTH in solution and under solvent free conditions

Entry	substrate	Product	Solvent Free			In CH_2Cl_2		
			Oxid/subst.	Time (h)	Yield%	Oxid/subst.	Time (h)	Yield%
1	$C_6H_5CH_2OH$	C_6H_5CHO	1.5	__b	95	2	__b	95
2	4-$ClC_6H_4CH_2OH$	4-ClC_6H_4CHO	1.5	0.17	100	2	0.3	80
3	4-$BrC_6H_4CH_2OH$	4-BrC_6H_4 CHO	1.5	0.17	100	2	0.3	78
4	4-$MeOC_6H_4CH_2OH$	4-$MeOC_6H_4$ CHO	1.2	__b	90	1.8	__b	75[c]
5	4-$MeC_6H_4CH_2OH$	4-MeC_6H_4 CHO	1.4	__b	90	2	0.2	85[c]
6	4-$O_2NC_6H_4CH_2OH$	4-$O_2NC_6H_4CHO$	2.2	0.25	95	3	0.5	90
7	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CHO$	2	0.17	90	2.5	0.5	80
8	$C_6H_5(CH_2)_2CH_2OH$	$C_6H_5(CH_2)_2CHO$	2	0.25	90	2.5	0.5	85
9	$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	1.5	0.25	85	2.5	0.5	78
10	$C_6H_5CH(OH)C_2H_5$	$C_6H_5COC_2H_5$	2	0.3	85	2.5	0.5	80
11	$C_6H_5CH(OH)C_6H_5$	$C_6H_5COC_6H_5$	2	0.3	100	2.5	0.5	100
12	n-$C_7H_{15}CH_2OH$	n-$C_7H_{15}CHO$	2	0.3	75[d]	2.5	0.5	65[d]
13	$C_5H_{11}CH(OH)C_2H$	$C_5H_{11}COC_2H$	2	0.5	80[d]	3	1	68[d]
14	p-hydroquinone	p-benzoquinone	1.5	0.5	95	2	1	83

[a]Isolated yield after column chromatography. [b]Reaction was completed immediately. [c]Reaction is Performed in CCl_4. [d]GC Yield

in 0.3 – 1h in solution and also under neat conditions at room temperature (Entries 12, 13, TABLE 1).

In conclusion, under solvent free conditions zirconium dichromate tetrahydrate (ZDCTH) is a more efficient oxidant and also versatile and bench top reagent for oxidation of primary and secondary benzylic alcohols. Less molar ratios of the oxidants are used under neat conditions in solution which makes this method more attracting for medium to large – scale operation. The rate and yields are usually higher under solvent free conditions than those reactions in solution.

EXPERIMENTAL

General

Chemicals were either prepared in our laboratories or were purchased from Fluka, Merck, B.D.H., Aldrich and Riedel Dehaen AG Chemical Companies. Products were Characterized by comparison of their physical data with those of authentic samples[8]. All yields refer to isolated product. Also all the solvents were completely dried and predistilled.

Preparation of Zirconium Dichromate Tetrahydrate (ZDCTH) [$Zr(Cr_2O_7)_2.4H_2O$)]

To a cold solution of chromic acid (472 g, 4 mol), prepared by the addition of chromium trioxide (400g, 4 mol) to a 3.4 molar solution of sulfuric acid (900 ml), zirconium chloride (233g, 1mol) was added in portions within 0.25 h. A dark reddish solution was produce. Evaporation of the solvent under vacuum afforded orange slurry, which was completely dried on the surface of a highly dried clay plate in the air to produce a brick – red powder with high stability (560 g, 85% yield). This compound is not hygroscopic and the proposed formula is in accord with the following evidences:

The comparison of the spectroscopic data (IR and UV spectra) of [$Zr(Cr_2O_7)_2.4H_2O$)] and $K_2Cr_2O_7$

IR and UV spectral data of $K_2Cr_2O_7$

IR: ν_{max} (KBr) ; 760 – 800 (b) ,890(s) , 910(m),930-970 (b) cm^{-1}. UV: (H_2O); 250 nm, 348 nm.

IR and UV spectral data of [$Zr(Cr_2O_7)_2.4H_2O$)]

IR: : ν_{max} (KBr) ;860 – 880 (b), 950 (s), 960(m), 1030 – 1200 (b), 1650 (b), 2500 –3500 (b) cm^{-1}.

UV: (H_2O); 248 nm, 340 nm

[$Zr(Cr_2O_7)_2.4H_2O$)] at 135°C loses its water which the weight lost amounts to four molecules of water.

General procedure for oxidation of alcohols with zirconium dichromate tetrahydrate (ZDCTH) in dichloromethane

To a solution of alcohol (1mmol) in CH_2Cl_2 (10ml)

in a round bottomed flask (25ml) equipped with a magnetic stirrer [$Zr(Cr_2O_7)_2.4H_2O$)] (1.8-3 mmol) was added. The reaction mixture was magnetically stirred for 0.2 –1h at room temperature. The progress of the reaction was monitored by TLC or GLC. The reaction mixture was filtered of a silica gel pad **(4g)** and the filter cake was further washed with ether (30ml). The combined filtrate were evaporated and the resulting residue was further purified by silica gel column chromatography and eluted with petrolium ether/ acetone (8/1) to afford the corresponding carbonyl compounds in good to high yields (TABLE 1).

General procedure for oxidation of alcohols with zirconium dichromate tetrahydrate (ZDCTH) under solvent free conditions

Amixture of alcohol (1mmol) and [$Zr(Cr_2O_7)_2.4H_2O$)] (1.2-2.2 mmlo) was prepared. The reaction mixture was magnetically agitated for immediately to 1h at room temperature. The progress of the reaction was monitored by TLC or GLC. To the resulting solid mixture, ether (30 ml) was added and filtered through a silicagel pad **(4g)** and the filter cake was washed further with ether (20ml). The combined filtrates were evaporated. The resulting residue was further purified by silica gel column chromatography and eluted with petrolium ether/ acetone (8/1) to afford the desired carbonyl compounds in good to high yields (TABLE 1).

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