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TRICHLOROMELAMINE/ZR(HSO_4)$_4$/KBR: AN EFFICIENT HETEROGENEOUS ALTERNATIVE FOR OXIDATION OF ALCOHOLS AND DIOLS

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TCM / Zr(HSO_4)$_4$ / KBr is a safe, versatile, cheap and efficient system for oxidation of alcohols and diols to carbonyl compounds.

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1. Introduction

Some specific features of *N*-halo reagents such as the high activity of the *N*-X bond and various modes of its splitting, determine and endorse their wide application in organic syntheses. Depending on the conditions, a number of highly reactive intermediates can be formed including halogen radicals, halogen cations, halogen anions, *N*-radicals, *N*-cations, *N*-anions and *etc*.

Consequently, *N*-halo reagents have the potential to promote important reactions such as halogenation, oxidation, and protection as well as formation of C-X, C-O, and C=O bonds. Chloroamines such as Trichloromelamine (TCM) are used as bleaching agents, disinfectants and bactericides, due to their function as chlorinating agents and oxidants.

Whereas carbonyl compounds are considered as useful synthetic intermediates, oxidation of alcohols to the corresponding carbonyl compounds is one of the most important reactions in organic synthesis.

Aldehydes and ketones have been prepared by the oxidation of corresponding alcohols with some oxidizing agents such as polymer supported TEMPO [1], Os/O_2 [2], Co(II)phtalocyanine [3], ruthenium / TEMPO [4], $KMnO_4$ [5,6], Silica sulfuric acid, $KBrO_3$ [7], H_2O_2/$FeBr_3$ [8], periodic acid or iodic acid in the presence of a catalytic amount of KBr [9], $H_{14}[NaP_5W_{30}O_{110}]$/$SiO_2$ [10], and heteropolyphosphatotungstate [11], among others. Recently more and more attention has been paid to the replacement of the traditional oxidation agents with positive halogen compounds such as I_2/TEMPO [12], NCS/N-*tert*-butylbenzenesulfenamide, [13] trichloroisocyanuric acid/$RuCl_3$ [14], NIS/CH_3COOAg [15], NBS/Bu_4NI [16], DABCO-Br_2 [17] and *N*,*N*-Dichloro-4-methylbenzenesulfonamide [18], as a green oxidant.

2. Experimental

General: Products were characterized by IR, ^{1}H-NMR, TLC and by comparison of their physical properties with those reported in the literature. IR spectras were run on a Bruker, Eqinox 55 spectrometer. ^{1}H-NMR were obtained using a Bruker Avans 400 MHz spectrometer and Bruker Avans 500 MHz spectrometer (DRX).

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General Procedure for Oxidation of Alcohols in the Presence of TCM/ $Zr(HSO_4)_4$/ KBr:

A mixture of alcohol, $Zr(HSO_4)_4$ and KBr was pulverized in a mortar or stirred in CH_2Cl_2 at room temperature or reflux. TCM was added in several portions and the reaction was continued until TLC analysis indicated a completed reaction (Table 2). The reaction mixture was then worked up by a dilution with cold *n*-hexane and filtration or cooling, filtration and washig with cold *n*-Hexane. Evaporation of solvent has given a product that has an acceptable purity for most of the purposes. In some cases that alcohol was as impurity in product, we have converted the carbonyl compound into corresponding semicarbazone derivative or purified by preparative TLC or column chromatography by using ether:petroleum ether (1:1)as an eluent.

3. Results and discussion

In this article, we describe a simple and efficient procedure for oxidation of alcohols to carbonyl compounds using a cheap and effective oxidant, Trichloromelamine (TCM). We have applied TCM in the presence of one acid as TCM activator and a salt as a catalyst. For this purpose, oxidation of benzyl alcohol into benzaldehyde was examined in the presence of TCM and various TCM activators and catalysts(Table 1)

Table 1. Ooxidation of benzyl alcohol (1mmol) in the presence of TCM, catalyst and an acid in CH_2Cl_2 at room temperature for 40 minutes.

Entry	Acid /mmol	Catalyst/mmol	TCM/mmol	Yield/%[a]
1	-	-	0.5	15
2	$Al(HSO_4)_4$ /0.1	-	0.5	50
3	$Al(HSO_4)_4$ /0.1	KBr /0.2	0.5	80
4	$Zr(HSO_4)_4$ /0.1	KBr /0.2	0.5	95
5	$Zr(HSO_4)_4$ /0.1	-	0.5	75
6	$SnCl_2$ /0.1	KBr /0.2	0.5	60
7	$AlCl_3$ /0.1	KBr /0.2	0.5	40
8	BF_3/SiO_2 /0.1	KBr/0.2	0.5	30
9	HCl[b] /0.1	KBr /0.2	0.5	-
10	H_2SO_4[b] /0.1	KBr /0.2	0.5	-
11	$ZnCl_2$ /0.1	KBr /0.2	0.5	40
12	$SbCl_3$ /0.1	KBr /0.2	0.5	40
13	SiO_2-SO_3H /0.1	KBr /0.2	0.5	60
14	$Zr(HSO_4)_4$ /0.1	KBr /0.2	0.2	50
15	$Zr(HSO_4)_4$ /0.1	KBr/0.2	0.33	60
16	$Zr(HSO_4)_4$ /0.1	KBr/0.2	0.4	95
17	$Zr(HSO_4)_4$ /0.1	KBr /0.2	0.66[c]	65
18	$Zr(HSO_4)_4$ /0.1	KBr /0.2	1[c]	65
19	$Zr(HSO_4)_4$ /0.03	KBr /0.2	0.4	45
20	$Zr(HSO_4)_4$ /0.05	KBr /0.2	0.4	70
21	$Zr(HSO_4)_4$ /0.07	KBr /0.2	0.4	95
22	$Zr(HSO_4)_4$ /0.16	KBr /0.2	0.4	95
23	$Zr(HSO_4)_4$ /0.07	NaBr /0.2	0.4	80
24	$Zr(HSO_4)_4$ /0.07	NH_4Cl /0.2	0.4	45
25	$Zr(HSO_4)_4$ /0.07	KCl /0.2	0.4	30
26	$Zr(HSO_4)_4$ /0.07	NaCl /0.2	0.4	45
27	$Zr(HSO_4)_4$ /0.07	KBr /0.1	0.4	75
28	$Zr(HSO_4)_4$ /0.07	KBr /0.15	0.4	83
29	$Zr(HSO_4)_4$ /0.07	KBr /0.25	0.4	96

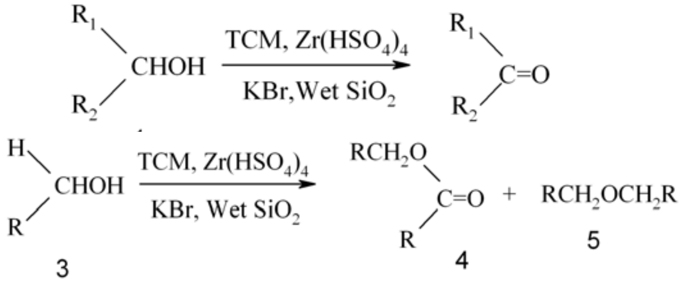
a) Isolated yield

b)Reaction was very fast and uncontrollable

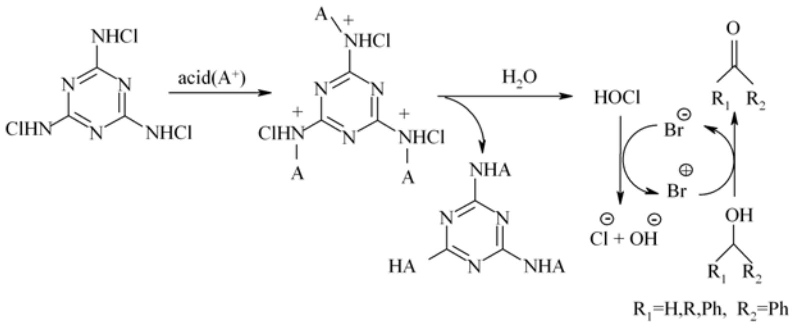
c) With high mmol of TCM, the side products were increased.

Because of the low nucleophilicity of oxygen in alcohols, in every molar ratio of benzyl alcohol to TCM, the yield of production has been low (15%). After checking a variety of acids as TCM activator we have found that $Zr(HSO_4)_4$ is the most effective activator for this reaction. By applying the TCM/$Zr(HSO_4)_4$ system, the yield of oxidation reaction was increased (75%). When we have applied Br^- as a catalyst, oxidation reaction occured with an improved yield (schem 1). In our proposed mechanism, Probably, $Zr(HSO_4)_4$ as an acid (A^+) forms an activated TCM, that can react with H_2O and form HOCl. Br^- from KBr can oxidize with HOCl and form Br^+ as a strong alcohol oxidizing agent (Scheme 2).

Scheme 1



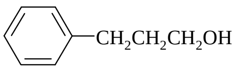
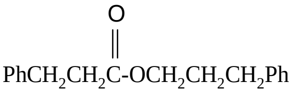
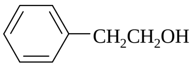
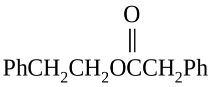
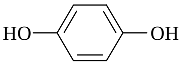
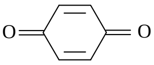
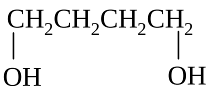
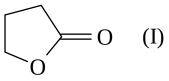
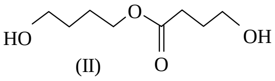
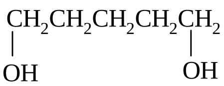
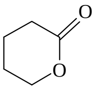
Scheme 2



Since the nucleophilicity of oxygen in alcohol and the conjugation of carbonyl group in products are important factors in the progression of this reaction, primary and secondary benzylic alcohols were oxidized with improved yields (80-95%). Primary aliphatic alcohols and diols were converted into the corresponding ethers, esters and lactones respectively (Table 2).

Table 2. Oxidation of alcohols (1mmol) to corresponding carbonyl compounds in the presence of TCM/Zr(HSO$_4$)$_4$/KBr/Wet SiO$_2$ [a]

Entry	Alcohol(1) R$_1$	R$_2$	Product(2)[a] R$_1$	R$_2$	TCM /mmol : $Zr(HSO_4)_4$ /mmol :KBr /mmol : Wet SiO_2 /g	condition	Time /h	Yield / %[b]
1	Ph	H	Ph	H	0.4:0.07:0.2:0.2	CH_2Cl_2, R.T.	0.75	95
2	Ph	Et	Ph	Et	0.4:0.0:/0:0	grinding	0.1	92
3	Ph	Me	Ph	Me	0.4:0.07:0:0	grinding	0.1	94
4	4-$NO_2C_6H_4$	H	4-$NO_2C_6H_4$	H	0.4:0.07:0.4:0.2	CH_2Cl_2, Reflux	22	92
5	4-Cl-C_6H_4	H	4-Cl-C_6H_4	H	0.4:0.07:0.2:0.2	CH_2Cl_2, R.T.	3	84
6	2,4-Cl_2-C_6H_4	H	2,4-Cl_2-C_6H_4	H	0.4:0.07:0.2:0.2	CH_2Cl_2, R.T.	4	92
7	3-OMe-C_6H_4	H	3-OMe-C_6H_4	H	0.4:0.07:0.2:0.2	CH_2Cl_2, Reflux	3.5	81
8	$(CH_2)_3$		$(CH_2)_3$		0.4:0.07:0.2:0.2	CH_2Cl_2, R.T.	6	83
9	4-*tert*-butyl-C_6H_4	H	4-*tert*-butyl-C_6H_4	H	0.4:0.07:0.2:0.2	CH_2Cl_2, R.T.	0.75	95
10	C_6H_4CO	Ph	C_6H_4CO	Ph	0.4:0.07:0.4:0.2	S.F., Heat	1	94
11	Ph	Ph	Ph	Ph	1:0.16:0.2:0.2	CH_2Cl_2, Reflux	1	91

Entry	Alcohol	Product	TCM/mmol: $Zr(HSO_4)_4$/mmol: KBr/mmol: Wet SiO_2 /g	condition	Time / h	Yield / %
12		 $PhCH_2CH_2\overset{\overset{O}{\|}}{C}\text{-}OCH_2CH_2CH_2Ph$	0.8/0.14/0.4/0.2	CH_2Cl_2, R.T.	55	60
		$PhCH_2CH_2CH_2OCH_2CH_2CH_2Ph$				25
13		 $PhCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_2Ph$	0.8/0.14/0.4/0.2	CH_2Cl_2, R.T.	10	45
		$PhCH_2CH_2OCH_2CH_2Ph$				35
14			0.4/0.07/0.2/0.2	CH_2Cl_2, R.T.	3	95
15	 $\underset{OH}{CH_2}CH_2CH_2\underset{OH}{CH_2}$	 (I)	0.8/0.14/0/0	CH_2Cl_2, R.T.	6	(I), 45 (II), 40
		 (II)			22	(I), 60 (II), 0
16	 $\underset{OH}{CH_2}CH_2CH_2CH_2\underset{OH}{CH_2}$		0.8/0.14/0/0	CH_2Cl_2, R.T.	28	80

a) All products are known and were identified by their melting point, IR and ^{1}H-NMR of carbonyl compounds or their semicarbazone derivatives according to SDBS or Sigmaaldrich website: http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi and http://www. Sigmaaldrich.com
b) Isolated yield

In sum, we report here that TCM/$Zr(HSO_4)_4$/KBr is an efficient and heterogeneous system for oxidation of alcohols to corresponding carbonyl compounds under solvent free condition with improved yields. Simple work up, clean reactions, scale up, generality and simplicity are some advantages of this method.

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