$[Ce(NO_3)_3]_3.H_2IO_6$: Efficient oxidation reactions under solvent-free conditions

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Efficient solvent-free oxidation of alcohols, deprotection and oxidative deprotection of trimethylsilyl ethers and oxidative deprotection of oximes using tris [trinitratocerium (IV)] paraperiodate (TTCPP) is reported.

Keywords: alcohols, oximes, solvent-free conditions, trimethylsilyl ethers, tris [trinitratocerium (IV)] paraperiodate

Cerium compounds are considered the most notable oxidants from the lanthanide group. There are several reviews,[1,2] books[3,4] and articles[5-8] reporting their synthetic applications on organic functions oxidation.

Recently, Firouzabadi et al have reported the synthesis and application of tris [trinitratocerium (IV)] paraperiodate (TTCPP) in the oxidation of different classes of organic compounds in dry refluxing benzene.[9,10] Although the yields of the obtained products using this reagent are relatively high, the method suffers from disadvantages such as unability of the reagent in the oxidation of aliphatic alcohols, long reaction times and relatively high oxidant-to-substrate ratio.

In view of this and in according to our experience in solvent-free reactions,[11-13] we decided to overcome on the above mentioned disadvantages by conduction the previous reactions in the absence of solvent. Herein, we report that TTCPP is able to oxidise alcohols efficiently under solvent-free conditions (Scheme 1).

The oxidation of various alcohols including primary and secondary benzylic and aliphatic ones was investigated in the absence of solvent at 90 °C using TTCPP. Yields and reaction times are given in Table 1. Over-oxidation of the products, using this method, was not observed.

Our investigations also indicated that deprotection and direct oxidative deprotection of trimethylsilyl ethers to their corresponding alcohols or carbonyl compounds, can be achieved efficiently in the presence of TTCPP under solvent-free conditions (Scheme 2).

$$R_1R_2CH_2OH \xrightarrow[\text{Solvent-free, 90 °C}]{\text{TTCPP(1 mmol)}} R_1R_2CO$$

Scheme 1

$$ROSiMe_3 \xrightarrow{\text{TTCPP (0.5 mmol)/ Solvent-free, r.t.}} ROH$$

$$R_1R_2CHOSiMe_3 \xrightarrow{\text{TTCPP (1 mmol)/ Solvent-free, 90 °C}} R_1R_2CO$$

Scheme 2

The pathway of the reaction is quite dependent upon the temperature, the reaction times and the oxidant-to-substrate ratio. Deprotection occurs at room temperature and in the presence of 0.5 molar equivalents of the reagent in few minutes (Table 2). It should be noted that direct conversion of trimethylsilyl ethers to their corresponding carbonyl compounds is performed by using 1 molar equivalents of the reagent at 90 °C in longer reaction times.

In order to show the efficiency of this method we have compared some of the results with some of those obtained by TTCPP in refluxing benzene (Table 3).[9, 10]

As shown in Table 3, by omitting the solvent, the reaction time and the oxidant to substrate ratio were reduced and the need for a toxic solvent is avoided.

Table 1 Solvent-free oxidation of alcohols using TTCPP

Entry	Substrate	Product	Time/h	Yield/%[a]
1	$PhCH_2OH$	$PhCHO$	0.25	95
2	$2\text{-}BrC_6H_4CH_2OH$	$2\text{-}BrC_6H_4CHO$	0.66	95
3	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CHO$	0.5	93
4	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CHO$	0.33	95
5	$2\text{-}MeC_6H_4CH_2OH$	$2\text{-}MeC_6H_4CHO$	0.25	90
6	$4\text{-}Me_3CC_6H_4CH_2OH$	$4\text{-}Me_3CC_6H_4CHO$	0.5	95
7	$2\text{-}NO_2C_6H_4CH_2OH$	$2\text{-}NO_2C_6H_4CHO$	3.5	80
8	$3\text{-}NO_2C_6H_4CH_2OH$	$3\text{-}NO_2C_6H_4CHO$	3	85
9	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CHO$	3	85
10	$PhCH(OH)CH_3$	$PhCOCH_3$	0.25	95
11	PhCH(OH)Ph	PhCOPh	0.33	90
12	PhCH(OH)COPh	PhCOCOPh	1	92
13	$PhCH_2CH_2CH_2OH$	$PhCH_2CH_2CHO$	0.75	95
14	$PhCH_2CH(OH)CH_3$	$PhCH_2COCH_3$	0.33	90
15	Cyclohexanol	Cyclohexanone	0.33	90
16	(-)-Menthol	(-)-Menthone	0.75	95
17	Borneol	Camphor	0.33	92
18	2-Adamantanol	2-Adamantanone	1.5	90
19	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCHO$	0.58	90

[a]Isolated yield.

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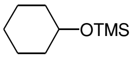
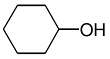
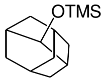
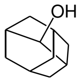
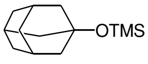
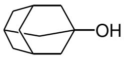
Table 2 Deprotection of trimethylsilyl ethers with TTCPP under solvent-free conditions

Entry	Substrate	Product	Time/min	Yield/%[a]
1	$PhCH_2OTMS$	$PhCH_2OH$	1	95
2	$2\text{-}BrC_6H_4CH_2OTMS$	$2\text{-}BrC_6H_4CH_2OH$	1	90
3	$4\text{-}ClC_6H_4CH_2OTMS$	$4\text{-}ClC_6H_4CH_2OH$	1	93
4	$4\text{-}Me_3CC_6H_4CH_2OTMS$	$4\text{-}Me_3CC_6H_4CH_2OH$	1	90
5	$4\text{-}NO_2C_6H_4CH_2OTMS$	$4\text{-}NO_2C_6H_4CH_2OH$	1	89
6	$2\text{-}NO_2C_6H_4CH_2OTMS$	$2\text{-}NO_2C_6H_4CH_2OH$	1	95
7	$2\text{-}MeC_6H_4CH_2OTMS$	$2\text{-}MeC_6H_4CH_2OH$	1	95
8	$4\text{-}PhCH_2OC_6H_4CH_2OTMS$	$4\text{-}PhCH_2OC_6H_4CH_2OH$	5	85
9	$4\text{-}MeOC_6H_4CH_2OTMS$	$4\text{-}MeOC_6H_4CH_2OH$	1	90
10	$Ph_2CHOTMS$	Ph_2CHOH	5	90
11	PhCOCH(OTMS)Ph	PhCOCH(OH)Ph	5	75
12	$PhCH_2CH_2CH_2OTMS$	$PhCH_2CH_2CH_2OH$	1	95
13	$PhCH_2CH(OTMS)CH_3$	$PhCH_2CH(OH)CH_3$	1	90
14			1	95
15			1	95
16			2	85
17	Me_3COTMS	Me_3COH	2	90

[a] Isolated yield.

$$R_1R_2C{=}NOH \xrightarrow[\text{Solvent-free, 90 °C}]{\text{TTCPP (2 mmol)}} R_1R_2CO$$

Scheme 3

We have found that TTCPP can also be used as an efficient reagent for the oxidative deprotection of oximes to their corresponding carbonyl compounds at 90 °C and under solvent-free conditions in good to high yields (Scheme 3). The results illustrated in Table 4 indicate that the reaction is successful for a variety of aliphatic and aromatic oximes.

Note that, unlike other oxidative hydrolytic methods, the major drawback of over-oxidation of the aldehydes to their carboxylic acids was not observed. Interestingly, α,β-unsaturated oximes underwent deoximation very efficiently without rearrangement of the carbon-carbon double bond and the reaction is essentially chemoselective. Furthermore, the phenolic hydroxy group was inert to this reagent and no by-product formation was observed (Table 4, entries 7, 8).

Table 3 Comparison of some of the results obtained by the using of TTCPP in solution (1)[9,10] and under solvent-free conditions (2)

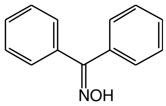
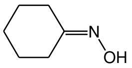
Entry	Substrate	Product	(Oxidant/substrate) (h) (Yield/%)	
			(1)	(2)
1	$PhCH_2OH$	PhCHO	(2)(0.5)(90–95)	(1)(0.25)(95)
2	PhCH(OH)Ph	PhCOPh	(2)(2)(90–95)	(1)(0.33)(90)
3	$2\text{-}NO_2C_6H_4CH_2OTMS$	$2\text{-}NO_2C_6H_4CH_2OH$	(3.5)(0.25)(90)	(0.5)(0.02)(95)
4	$PhCH_2CH_2CH_2OTMS$	$PhCH_2CH_2CH_2OH$	(5)(0.25)(90)	(0.5)(0.02)(95)
5	$Ph_2CHOTMS$	Ph_2CO	(4.5)(3)(55)	(1)(0.33)(95)
6	$4\text{-}MeOC_6H_4CH_2OTMS$	$4\text{-}MeOC_6H_4CHO$	(3)(3.5)(90)	(1)(0.42)(90)

Table 4 Oxidative deprotection of oximes under solvent-free conditions

Entry	Substrate	Product	Time/min	Yield/%[a]
1	$4\text{-}ClC_6H_4CH{=}NOH$	$4\text{-}ClC_6H_4CHO$	5	97
2	$2\text{-}ClC_6H_4CH{=}NOH$	$2\text{-}ClC_6H_4CHO$	10	95
3	2,4-Dichlorobenzaldoxime	2,4-Dichlorobenzaldehyde	20	96
4	$4\text{-}BrC_6H_4CH{=}NOH$	$4\text{-}BrC_6H_4CHO$	15	95
5	$4\text{-}PhC_6H_4CH{=}NOH$	$4\text{-}PhC_6H_4CHO$	10	95
6	$2\text{-}NO_2C_6H_4CH{=}NOH$	$2\text{-}NO_2C_6H_4CHO$	15	95
7	4-Nitrosalicylaldoxime	4-Nitrosalicylaldehyde	15	93
8	2-Nitrosalicylaldoxime	2-Nitrosalicylaldehyde	15	95
9	1-Naphthaldehyde oxime	1-Naphthaldehyde	35	90
10	$4\text{-}MeC_6H_4C({=}NOH)Me$	$4\text{-}MeC_6H_4C(O)Me$	5	95
11	$4\text{-}BrC_6H_4C({=}NOH)CH_2Br$	$4\text{-}BrC_6H_4C(O)CH_2Br$	10	95
12	$4\text{-}\ NO_2C_6H_4C({=}NOH)Me$	$4\text{-}\ NO_2C_6H_4C(O)Me$	20	90
13	$Ph_2C{=}NOH$	Ph_2CO	25	95
14	$PhCH{=}CHCH{=}NOH$	$PhCH{=}CHCHO$	15	92
15	$4\text{-}NO_2C_6H_4CH{=}CHCH{=}NOH$	$4\text{-}NO_2C_6H_4CH{=}CHCHO$	30	85
16	$PhCH_2C({=}NOH)Me$	$PhCH_2C(O)Me$	10	95
17	Cyclohexanone oxime	Cyclohexanone	10	92
18	2-Adamantanone oxime	2-Adamantanone	15	95

[a] Isolated yield.

Table 5 Regeneration of carbonyl compounds from their corresponding oximes using TTCPP (**1**) in comparison with ozone (**2**),[14] sodium perborate (**3**)[15] and γ-picolinium chlorochromate (**4**).[16]

Entry	Substrate	(Oxidant / Substrate)(min)(Yield/%)(T/°C)			
		(1)	(2)	(3)	(4)
1		(2)(25)(95)(90)		(4)(300)(87)(95)	(1.5)(240)(95)(25)
2		(2)(10)(92)(90)	(–)(120)(94)(-25)	(4)(300)(80)(95)	(1.5)(900)(75)(25)

In order to show the efficiency of TTCPP in the oxidative deprotection of oximes, Table 5 compares some of the results with some of those reported in the literature.[14-16]

The mildness of the reaction conditions, high efficiency, chemoselectivity, approximately short reaction times, reasonable yields of the products, simple and clean work-up and solvent-free reaction conditions are among the outstanding advantages of this new method.

Experimental

General

Chemicals were purchased from Merck, Fluka, BDH and Aldrich Chemical Companies. Products were separated and purified by different chromatography techniques, and were identified by the comparison of their m.p., b.p., IR and ^{1}H NMR data with those reported for the authentic samples. All yields refer to the isolated products. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on Merck kisselgel 60H.

Oxidation of alcohols and trimethylsilyl ethers to their corresponding carbonyl compounds.

General procedure

A mixture of the substrate (1 mmol) and TTCPP (1 mmol) was shaken in an oil bath (90 °C) for the specified time (Table 1). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (5 ml) and filtered and the solid residue was washed with CH_2Cl_2 (3 ml).Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding cabonyl compounds in good to high yields.

Deprotection of trimethylsilyl ethers to their corresponding alcohols.

General procedure

A mixture of the substrate (1 mmol) and TTCPP (0.5 mmol) was shaken at room temperature for the specified time (Table 2). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (5 ml) and filtered and the solid residue was washed with CH_2Cl_2 (3 ml). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding cabonyl compounds in good to high yields.

Oxidative deprotection of oximes to their corresponding carbonyl compounds.

General procedure

A mixture of the substrate (1mmol) and TTCPP (2 mmol) was heated in an oil bath (90 °C) for the specified time (Table 4). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (5 ml) and filtered. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

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