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NOTE

Oxidation of Benzylic Alcohols by Tris[Trinitrato Ce(IV)] Paraperiodate in Solvent Free Condition

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Tris[trinitratocerium(IV)] paraperiodate has been used for the oxidation of benzylic alcohols to their corresponding carbonyl compounds in solvent free condition with high yields.

Among lanthanide reagents, cerium(IV) compounds represent the most notable oxidants in organic synthesis.[1,2] In particular, ceric ammonium nitrate (CAN) has been utilized extensively for a variety of oxidative transformations.[2] The chemistry of Ce(IV) oxidation of organic compounds is dominated by radical and radical cations.[2–6] Since the fate of these radical intermediates and the nature of the oxidant can affect the nature of the organic product, new Ce(IV) reagents were synthesised and applied for different types of transformations.[1,2] Among these reagents tris[trinitratiocerium (IV)] paraperiodate was used as an efficient reagent for oxidation of different functional groups and ring opening of epoxides.[7,9]

In this paper we wish to report that tris[trinitratocerium(IV)] paraperiodate (TTCPP) can act as a suitable reagent for the oxidation of benzylic alcohols to their corresponding carbonyl compounds in solvent free condition (Table-1). In an easy procedure the reactants mixed together in a mortar and stood for the appropriate period (Table-1), at 80°C, without any further agitation. This method is not suitable for the oxidation of aliphatic alcohols, *e.g.*, 1-phenyl-2-propanol and 3-phenyl-1-propanol (Table-1).

In order to compare the obtained results with those performing in solution we tried to study the oxidation reactions in CH_2Cl_2. As shown in the Table-1 there are appreciable differences between the results obtained in solution in neat condition.

In conclusion, omitting the solvent in oxidation of benzylic alcohols by TTCPP changes the reaction time and product yield significantly while the need of using the solvent is suppressed and work up procedure becomes easier.

All products were characterized through comparison of their spectral and physical data with those of the known samples.[10–12] The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. Products were separated and purified by different chromatography

techniques, and were also identified by the comparison of their mp, IR and NMR spectra, bp and refractive index with those reported for the authentic samples.

TABLE-1
OXIDATION OF BENZYLIC ALCOHOLS BY TTCPP, $[(NO_3)_3Ce]_3 \cdot H_2IO_6$, IN DICHLOROMETHANE[a] OR SOLVENT FREE CONDITION[b]

Substrate	Product	Solvent free oxidation		Oxidation in CH_2Cl_2	
		Time (h)	yield (%)	Time (h)	yield (%)
Benzyl alcohol	Benzaldehyde	1.10	85	0.50	87
4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	0.58	90	15.00	85
2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	2.00	82	15.00	70
4-Bromobenzyl alcohol	4-Bromobenzaldehyde	1.90	86	7.70	90
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	0.80	85	9.30	84
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	0.70	90	0.75	62
4-Benzyloxybenzyl alcohol	4-Benzyloxybenzaldehyde	1.70	80	6.20	60
Diphenyl carbinol	Benzophenone	1.90	82	4.20	65
1-Phenyl ethanol	Acetophenone	1.30	92	15.00	70
1-Phenyl-2-propanol	Phenylacetone	3.20	–[c]	6.30	–[c]
3-Phenyl-1-propanol	3-Phenylpropanal	7.00	–[c]	8.50	–[c]

[a] The reaction was performed under refluxing condition.
[b] The reaction was performed at 80°C.
[c] Mixture of products were produced.

General Procedure for Oxidation of Benzylic Alcohols by TTCPP Under Solvent Free Condition

TTCPP (1 mmol) was added to benzylic alcohol (1 mmol) in a mortar. Starting materials were mixed and stood together for the appropriate period (Table-1) at 80°C. The reaction was monitored by TLC. After completion of the reaction, CH_2Cl_2 (10 mL) was added and the mixture was filtered. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compound in good to high yields (Table-1).

General Procedure for Oxidation of Benzylic Alcohols by TTCPP in CH_2Cl_2

To a solution of benzylic alochol (1 mmol) in CH_2Cl_2 (3 mL), TTCPP (1 mmol) was added and the mixture was refluxed for the appropriate time (Table-1). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled, filtered and the solid residue was washed with CH_2Cl_2 several times (2×5 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the correponding carbonyl compounds (Table-1).

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