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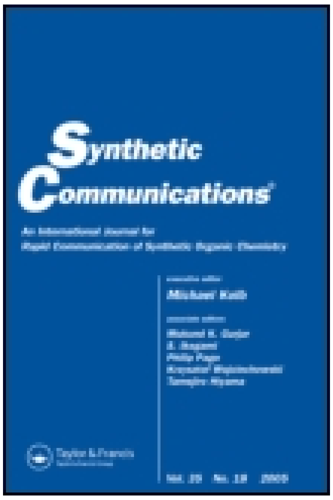

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$[NO_3)_3Ce]_3.H_2IO_6$: AS A VERSATILE AND EFFICIENT REAGENT FOR CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS UNDER HETEROGENEOUS AND NON-AQUEOUS CONDITIONS

F. Shirini [a] & M. R. Azadbar [a]
[a] Department of Chemistry, Faculty of Science , Gulian University , Rasht, Iran
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$[(NO_3)_3Ce]_3.H_2IO_6$: AS A VERSATILE AND EFFICIENT REAGENT FOR CLEAVAGE OF CARBON–NITROGEN DOUBLE BONDS UNDER HETEROGENEOUS AND NON-AQUEOUS CONDITIONS

F. Shirini* and M. R. Azadbar

Department of Chemistry, Faculty of Science,
Gulian University, Rasht, Iran

ABSTRACT

Oximes, hydrazones and semicarbazones of benzylic aldehydes and ketones undergo facile cleavage to the corresponding carbonyl compounds by *tris*[tri-nitratocerium(IV)]paraperiodate, $[(NO_3)_3Ce]_3.H_2IO_6$, in good to high yields.

Derivatives of carbonyl compounds such as oximes, hydrazones and semicarbazones are highly crystalline and very useful for the characterization and purification of carbonyl compounds. Regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry.

The classical method for the cleavage of oximes to aldehydes and ketones includes acid hydrolysis which is not suitable for acid sensitive

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*Corresponding author.

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compounds.[1] Several oxidative deoximation methods have been developed which have found some advantages over the classical hydrolysis methods.[2–5] Little attention has been paid to the oxidative cleavage of hydrazones and semicarbazones and only a few reports are available dealing with the conversion of these derivatives to their corresponding carbonyl compounds.[6–8]

In this communication we wish to report that *tris*[trinitrato Ce(IV)]-paraperiodate, $[(NO_3)_3Ce]_3.H_2IO_6$, a previously reported oxidizing agent,[9–11] is able to perform the cleavage of carbon–nitrogen double bonds of benzylic oximes, hydrazones and semicarbazones in refluxing acetonitrile.

Our experiments show that benzylic oximes, hydrazones and semicarbazones are converted to their corresponding aldehydes and ketones in low reaction times and in good to high yields (Table 1). In Table 2 the results of our experiments are compared with some of those reported in literature. This methodology is not recommended for the cleavage of aliphatic carbon–nitrogen double bonds (Table 1, entries 23, 24).

In summary, *tris*[trinitratocerium(IV)]paraperiodate is an effective and convenient reagent for converting benzylic oximes, hydrazones and semicarbazones to their corresponding carbonyl compounds. A full research, based on this method, conserning cleavage of carbon–nitrogen double bonds in other classes of organic compounds is under way.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka, BDH and Aldrich chemical companies. All oximes, hydrazones and semicarbazones were prepared using standard synthetic methods.[12,13] Products were separated and purified by different chromatography techniques, and were also identified by the comparison of their mp, IR, NMR, bp and refractive index with those reported for authentic samples.

General Procedure

A solution of the substrate (1 mmol) in acetonitrile (3 mL) was treated with 0.5–1 molar equivalent of reagent and the mixture was refluxed for 5–90 min. The progress of the reaction was monitored by TLC or GLC. The reaction mixture was filtered and the solid residue was washed by acetonitrile (9 mL). Evaporation of the solvent followed

Table 1. Regeneration of Benzylic Aldehydes and Ketones from Corresponding Oximes, Hydrazones, and Semicarbazones with $[(NO_3)_3Ce]_3.H_2IO_6$ in Refluxing CH_3CN

Entry	Substrate	Product	Oxi. Sub.	Time (min)	Yield (%)
1	Acetophenone oxime	Acetophenone	0.5	5	93
2	Benzophenone oxime	Benzophenone	0.5	5	95
3	4-Methylacetophenone oxime	4-Methylacetophenone	0.5	5	87
4	4-Chlorobenzaldoxime	4-Chlorobenzaldehyde	0.5	15	90
5	4-Nitrobenzaldoxime	4-Nitrobenzaldehyde	0.5	15	75
6	Furfural oxime	Furfural	0.5	15	75
7	3-Nitrobenzaldoxime	3-Nitrobenzaldehyde	0.5	15	70
8	4-Methylacetophenone hydrazone	4-Methylacetophenone	1	30	85
9	Benzaldehyde hydrazone	Benzaldehyde	1	5	95
10	4-Methylbenzaldehyde hydrazone	4-Methylbenzaldehyde	1	5	90
11	4-Chlorobenzaldehyde hydrazone	4-Chlorobenzaldehyde	1	20	90
12	4-Methoxybenzaldehyde hydrazone	4-Methoxybenzaldehyde	1	60	95
13	4-Nitrobenzaldehyde hydrazone	4-Nitrobenzaldehyde	1	90	95
14	3-Nitrobenzaldehyde hydrazone	3-Nitrobenzaldehyde	1	70	90
15	Benzaldehyde dimethylhydrazone	Benzaldehyde	1	15	90
16	4-Chlorobenzaldehyde dimethylhydrazone	4-Chlorobenzaldehyde	1	35	80
17	Benzaldehyde phenylhydrazone	Benzaldehyde	1	30	75
18	Benzaldehyde semicarbazone	Benzaldehyde	1	5	90
19	Acetophenone semicarbazone	Acetophenone	1	40	85
20	Benzophenone semicarbazone	Benzophenone	1	15	87
21	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	1	15	85
22	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	1	90	90
23	Camphor oxime	Camphor	0.5	45	–[a]
24	Cyclohexanone semicarbazone	Cyclohexanon	1	90	–[a]

[a] Mixture of products.

Table 2. Comparison of Some of the Results Obtained from $[(NO_3)_3Ce]_3.H_2IO_6$ (**1**) and Some of Those Reported with Methyl Ammonium Chlorochromate Adsorbed on Alumina (**2**),[3] Sodium Perbromate (**3**),[4] Pyridinium Chlorochromate (**4**),[5] and Ozone (**5**)[5]

			Yield (%)				
Entry	Substrate	Product	1	2	3	4	5
1	Acetophenone oxime	Acetophenone	93	76	88	55	96
2	Benzophenone oxime	Benzophenone	95	61	87	55	95
3	Benzaldehyde phenylhydrazone	Benzaldehyde	75	–	–	65	–
4	Acetophenone semicarbazone	Acetophenone	85	–	–	15	–

by column chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yields.

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