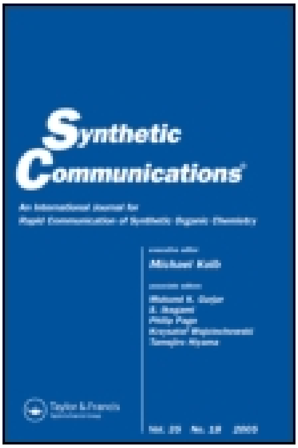

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OXIDATION OF BENZYL ALCOHOLS AND ACYLOINS WITH $(NO_3)_3CeBrO_3$

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OXIDATION OF BENZYL ALCOHOLS AND ACYLOINS WITH $(NO_3)_3CeBrO_3$

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ABSTRACT

Trinitratocerium(IV) bromate (TNCB) was prepared by the reaction of cerium(IV) ammonium nitrate (CAN) with sodium bromate. The oxidizing ability of this compound was observed in the oxidation of benzyl alcohols and acyloins to the corresponding carbonyl compounds.

Cerium(IV) compounds represent the most notable oxidants among lanthanide reagents. In particular, ceric ammonium nitrate (CAN) has been utilized extensively for a variety of oxidative transformations.[1] Unfortunately oxidation with this reagent suffers from various disadvantages.[2] This reagent is not effective in the oxidation of benzyl alcohol in refluxing acetonitrile and after 2.5 h, benzyl alcohol was isolated intact.[3]

Sodium bromate which has also been used in the oxidation of organic compounds,[4] was also quite ineffective in the oxidation of benzyl alcohol.[3]

In this communication we report a synergistic effect between ceric ammonium nitrate (CAN) and sodium bromate in trinitratocerium(IV) bromate, $(NO_3)_3CeBrO_3$,[5–7] which is quite stable and capable of oxidizing benzyl alcohols and acyloins in refluxing acetonitrile.

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Table 1. Oxidation of Benzyl Alcohols and Acyloins with TNCB in Refluxing Acetonitrile

Entry	Substrate	Oxidant Substrate	Reaction Time (h)	Product	Yield %
1	Benzyl alcohol	4	2.5	Benzaldehyde	92
2	2-Chlorobenzyl alcohol	4	5.5	2-Chlorobenzaldehyde	90
3	4-Chlorobenzyl alcohol	4	5	4-Chlorobenzaldehyde	85
4	4-Bromobenzyl alcohol	4	7.5	4-Bromobenzaldehyde	86
5	4-Methyl benzyl alcohol	4	6.5	4-Methylbenzaldehyde	85
6	1-Phenyl ethanol	6	2.5	Acetophenone	82
7	Benzoin	1	0.25	Benzil	92
8	4,4′-Dimethoxybenzoin	1	0.25	4,4′-Dimethoxybenzil	85
9	Furoin	1	0.75	Furil	90

Different benzyl alcohols were oxidized to the corresponding benzaldehydes (Table 1). Acyloins, as α-hydroxy ketones, were also effectively oxidized to the corresponding diketones with quantitative amounts of the reagent, in low reaction times and in high yields (Table 1).

It is noted that the over-oxidation of the produced benzaldehydes to their corresponding benzoic acid and C-C bond cleavage of the acyloins, which are the common reactions in the oxidations with ceric ammonium nitrate,[8,9] were not observed during the course of the reaction.

In order to show the synergistic effect in TNCB we have compared some of the results with some of those obtained by CAN and $NaBrO_3$ in the same conditions[3] (Table 2).

The ease of preparation, handling, stability and mildness of this compound makes it a particular bench reagent. Full investigations of the oxidation of different classes of organic compounds with this reagent are under way.

EXPERIMENTAL

Preparation of Trinitratocerium(IV) Bromate(TNCB)

To a solution of sodium bromate (0.151 g, 1 mmol) in water (10 ml) at 70°C a solution of CAN (0.548 g, 1 mmol) in water (3 ml) was added with vigorous stirring. The resulting mixture was stirred at 70°C for 30 min, and cooled to room temperture, whereupon a yellow precipitate was produced.

Table 2. Comparison of Some of the Results Obtained by the Oxidation with TNCB(1) with Some of Those Obtained by CAN(2) and $NaBrO_3$ in Refluxing Acetonitrile

			(Oxidant/Substrate)(h)(Yield%)		
Entry	Substrate	Product	(1)	(2)	(3)
1	Benzyl alcohol	Benzaldehyde	(4)(2.5)(92)	(4)(2.5)(0)	(4)(2.5)(0)
2	Furoin	Furil	(1)(0.75)(90)	(1)(2)(0)	(1)(2)(0)

This precipitate was collected by filteration, washed with water and acetone several times and dried in vacuo (0.317 g, 70%).

General Procedure for the Oxidation of Benzyl Alcohols and Acyloins with TNCB

A solution of the substrate (1 mmol) in acetonitrile (3 ml) was treated with 1–6 molar equivalents of the reagent and the reaction mixture was refluxed with stirring for 0.25–6 h. 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 acetonitrile several times (2×5 ml). Evaporation of the solvent followed by column chromatography on silica gel, gave the corresponding carbonyl compounds from good to high yields. The product of each reaction was identified by its refractive index (n_D) or mp, IR and NMR spectra and was compared with those reported for the authentic samples.[10–12]

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