# Benzylic oxidation of aromatics with cerium(IV) triflate; synthetic scope and mechanistic insight

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The synthetic utility of cerium(iv) triflate Ce(OTf)<sub>4</sub> as a reagent for benzylic oxidation has been tested for a variety of aromatic compounds. Insight is provided into various factors that govern these oxidations and their progress. It has been shown that the mode of preparation of Ce(OTf)<sub>4</sub> and the % H<sub>2</sub>O present in the sample have a marked influence on oxidation ability. A variety of mono- and dialkylbenzenes, haloalkylbenzenes, bicyclic and tricyclic ring systems, and alkoxybenzenes have been surveyed. The method offers an easy to perform one-pot reaction for the room temperature synthesis of aromatic ketones and aldehydes from aromatics and has the potential to find wider application.

# Introduction

Oxidation at benzylic positions is a fundamental synthetic transformation, which depending on the reagent and conditions, converts alkylaromatics to alcohols, aldehydes, ketones, or carboxylic acids.<sup>1,2</sup> Over the years, a wide variety of reagents have been developed and tested; among them metal oxides and lanthanide reagents, in particular Ce(IV) compounds, have been the dominant players.<sup>3-8</sup> Benzylic methylene and methyl groups can be transformed into carbonyl functions by using cerium ammonium nitrate "CAN", typically in hot HOAc, HNO3 or HClO<sub>4</sub>. The scope of these reactions has been reviewed.<sup>4-7</sup> In MeCN solvent, under thermal or photochemical conditions, side-chain nitration could compete with oxidation.9,10 The utility of CAN-promoted benzylic oxidation is limited to activating substituents and the yields diminish when an electron withdrawing group is introduced.<sup>4</sup> Oxidation of mesitylene with cerium(IV) trifluoroacetate in TFA produced a mixture of the diarylmethane, biaryl and the ester.<sup>11</sup> In search of more powerful, chemoselective, oxidants cerium(IV) methanesulfonate and cerium(IV) triflate were generated electrochemically and used in situ for oxidation of simple alkylbenzenes.<sup>12</sup> Imamoto et al.<sup>13</sup> first prepared and isolated cerium(IV) triflate via cerium carbonate-TfOH and provided a limited number of examples for converting primary benzylic alcohols to aldehydes, and alkylbenzenes to aldehydes or ketones.<sup>13a</sup> Aldrich subsequently introduced "cerium trifluoromethanesulfonate hydrate" into its catalog. Several recent studies utilized cerium triflate for epoxide ring opening,<sup>14</sup> oxidation of α-methylpyrrole,<sup>15</sup> esterification,<sup>16</sup> and biaryl synthesis,<sup>17</sup> however there has been no detailed study of benzylic oxidation mediated by  $Ce(OTf)_4$ , in order to evaluate its scope and limitation, and to determine various factors that influence this chemistry.

#### **Results and discussion**

#### Background

In the work of Imamoto *et al.*,<sup>13a</sup> Ce(OTf)<sub>4</sub> was prepared from cerium carbonate and triflic acid. The water content in the isolated sample was determined to be 3.70%. Oxidation reactions were performed in MeCN–H<sub>2</sub>O (1 : 1) as solvent, with a Ce(OTf)<sub>4</sub> to arene molar ratio of 4.5:1 for alkylbenzene to aldehyde (or ketone) conversion and 2.5:1 for benzylic alcohol

to aldehyde conversion. There was no mention of the presence of other products.

#### Initial studies

Several batches of cerium triflate were prepared using a modification of the procedure described by Imamoto et al. 13a in which ceric carbonate (via CAN and aqueous potassium carbonate) was reacted with four equivalents of TfOH either directly or by using 1,1,2-trichlorotrifluoroethane (Freon-113) as solvent, and the resulting cerium triflate was isolated and dried. Using ethylbenzene oxidation as benchmark, a series of reactions were carried out in MeCN solvent in which Ce(OTf)<sub>4</sub> : arene molar ratios were either 4.5:1 or 2.5:1. For each set, the reaction times were varied in independent experiments conducted at room temperature. In several runs the oxidation was carried out at ca. 65-70 °C. GC analysis showed that apart from acetophenone, 2-phenylethanol was also present. Furthermore, it was found that the use of a 4.5 fold excess of Ce(OTf)<sub>4</sub> was usually unnecessary, as similar conversions could be achieved with a ca. 2.5-2.0 fold excess of Ce(OTf)<sub>4</sub>. In experiments where the reaction mixture was heated, 2-phenylethanol became the predominant product. These studies also illustrated that the outcome of Ce(OTf)<sub>4</sub> oxidation (product composition and % conversion) was variable from batch to batch.

#### Oxidation power versus % H<sub>2</sub>O in Ce(OTf)<sub>4</sub>

In order to determine to what extent the water content influences oxidation power, thermal gravimetric analysis (TGA) was performed on several samples prepared with or without employing Freon solvent. Based on these measurements, the % water content in ceric triflate was estimated in the 14–22% range. Samples prepared using Freon solvent contained less water, some as low as 1.5%. Table 1 summarizes the relationship between % H<sub>2</sub>O and product distribution for oxidation of ethylbenzene. Prolonged reaction times and/or more anhydrous ceric triflate led to the formation of substantial amounts of alcohol. Employing a 2 : 1 Ce(OTf)<sub>4</sub> to arene molar ratio, the maximum yield of PhCOMe that could be realized was 78% (24 hours stirring at rt).

In a control experiment EtPh was first reacted with 2 mol equivalents of ceric triflate (a batch containing 16.6%  $H_2O$ ). After 2 hours stirring at rt an additional two equivalents of Ce(OTf)<sub>4</sub> were added. This led to near quantitative conversion



					%Yield	
Time	Temp/°C	% H <sub>2</sub> O in Ce(OTf) <sub>4</sub>	Ce(OTf) <sub>4</sub> /mmol	Substrate/mmol	<b>1</b> a	1b
47 h	rt	1.50	0.680	0.340	9.5	85.7
27 h	rt	13.00	0.680	0.340	44.4	9.8
4 h	rt	6.50	0.680	0.340	2.3	1.8
29 h	rt	$1.50^{a}$	0.680	0.340	4.2	32.5
3.5 h	rt	16.06	0.680	0.340	15.0	34.0
20 h	rt	16.06	0.680	0.340		100
45 h	rt	16.06	1.017	0.340	22.0	20.0
46 h	rt	13.00	0.680	0.340	59.0	36.0
3.5 h	65	16.06	0.680	0.340	8.3	9.6
2 h	rt	$1.50^{b}$	1.530	0.340		
20 min	rt	13.00	0.680	0.340	40.0	58.0
22 h	rt	12.40	0.680	0.340	15.7	23.4
24 h	rt	1.50	9.50	4.70	4.8	93.7 <sup>c</sup>
24 h	rt	14.00	5.60	2.80	78.8	17.8
22 h	rt	23.03	0.680	0.340	30.6	
17 h	rt	16.40	0.700	0.350	67.0	7.0
19.5 h	rt	16.40	1.40	0.350	99.7	_

<sup>*a*</sup> A water–acetonitrile (1 : 1) solvent system was employed. <sup>*b*</sup> Water was added *via* a micropipette to the reaction in a 2 : 1, water : substrate ratio. <sup>*c*</sup> The product was isolated and identified by <sup>1</sup>H NMR and <sup>1</sup>H–<sup>1</sup>H COSY.

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					%Yield	
EtPh oxidation at rt	Time/h	% H <sub>2</sub> O in Ce(OTf) <sub>4</sub>	Ce(OTf) <sub>4</sub> /mmol	Substrate/mmol	<b>1</b> a	1b
Aldrich #1	27.5	11.10	0.680	0.340	14.6	4.6
Aldrich #1	21	$11.10^{a}$	0.632	0.316	5.0	
Aldrich #2	28	12.98	0.680	0.340	15.4	4.4
Aldrich #2	19.5	$17.60^{b}$	0.331	0.165	7.4	90.3

<sup>*a*</sup> Water was added *via* a micropipette to the reaction mixture in a 2:1, water : substrate ratio. <sup>*b*</sup> The Aldrich sample was rehydrated using the indicated procedure.

to PhCOMe (99.7%) with only a trace of alcohol. The water content in two commercial samples of ceric triflate was estimated in the 11-13% range (TGA). The commercial samples proved to be inferior relative to the synthesized samples for EtPh oxidation (Table 2). In an effort to modify the oxidation power of the commercial samples and to bring them in par with those synthesized, they were "rehydrated" either by adding water to MeCN in the oxidation reactions, or by adding water to the Ce(OTf)<sub>4</sub> in MeCN without the aromatic substrate and by re-drying, while monitoring via TGA analysis until the water content was in the "optimal" range. Using EtPh oxidation as a probe, the former approach led to poor conversion whereas the latter led to predominant formation of 2-phenylethanol (90%; with 17.6% water in ceric triflate, after ca. 20 h stirring at rt). It is clear that the success of benzylic oxidation with Ce(OTf)<sub>4</sub> strongly depends on a "correct" preparative procedure for the reagent. Samples prepared according to methods reported herein (see Experimental section) with optimal water content proved to be efficient oxidants.

#### Monitoring the course of oxidation

Using EtPh and a Ce(OTf)<sub>4</sub> to arene ratio of 2:1, the progress of oxidation was monitored by GC. Aliquots were withdrawn beginning after 3 minutes, quenched and analyzed. The outcome is summarized in Table 3. The results show that initial oxidation is highly selective, rapidly producing PhCOMe (no alcohol is observed), which reached 78.4% after 1 h at rt. Longer reaction times led to the appearance of alcohol which slowly increased over time at the expense of unreacted EtPh. Thus an efficient  $Ce(OTf)_4$  promoted oxidation is followed by a slow oxidation of the unreacted substrate up to the alcohol level. The later "sluggish" process is probably promoted by the formed Ce(III) triflate.

#### Survey of synthetic scope

In order to establish potential synthetic utility, the oxidation of a series of aromatic compounds was investigated.

Isomeric fluoro- and chlorotoluenes (Table 4). 2-Fluorotoluene gave 2-fluorobenzaldehyde as the major and 2-fluorobenzyl alcohol as minor product. With 4-fluorotoluene, chemoselectivity was variable. Using a Ce(OTf)<sub>4</sub> sample with 22% H<sub>2</sub>O, quantitative conversion to the alcohol was observed. 4-Fluorobenzyl alcohol was further oxidized to the aldehyde in quantitative yield by addition of an additional 2 equivalents of ceric triflate after stirring at rt for 22 h.

For chlorotoluenes, the *ortho* isomer gave a mixture of aldehyde and alcohol products, favoring the alcohol. An independent run with a shorter reaction time led to only *ca.* 24% conversion in which the aldehyde was the major product. The *meta* isomer gave either low conversion or no reaction and the *para* isomer did not react.

Diphenylmethane and bibenzyl (Tables 5 and 6). By using a 2:1 ceric triflate to arene ratio, PhCOPh (61.2%) and

diphenylmethanol (11.6%) were both produced, whereas by using a 1 : 1 ratio only PhCOPh was present (65%) and no alcohol could be detected. With bibenzyl, a low yield of the monoketone was formed along with some PhCOMe (no diketones were obtained).

Isomeric ethylmethylbenzenes (ethyltoluenes) (Tables 7 and 8). A strong preference for benzylic methylene oxidation relative to benzylic methyl is established. For 4-ethyltoluene, three independent experiments were performed, showing rather significant variation in product distribution with the main products in all cases being *p*-methylacetophenone and the corresponding alcohol. An experiment with a 3 min reaction time produced a 40% yield of the ketone. With 2-ethyltoluene, prolonged reaction times led to increased amounts of alcohol and some *o*-ethyltolualdehyde was also formed.

Isomeric diethylbenzenes (Tables 9 and 10). With p-diethylbenzene (ceric triflate to arene ratio 2:1), all four possible oxidation products were formed. Employing a 4:1 ratio, the selectivity was higher with the monoketone comprising 61.3% of the reaction mixture. With *m*-diethylbenzene two independent reactions were run. With a very short reaction time and gentle heating, a 48% yield of the monoketone was obtained, whereas longer reaction times at rt led to the formation of both mono- and diketone and the former was predominant.

 Table 3
 Monitoring the oxidation progress.



Table 4 Oxidation of halotoluene isomers

*n***-Butylbenzene (Table 11).** Two independent runs were performed. In one case the ketone and the alcohol were both formed with an overall conversion of 79%. In the other case no alcohol was found but the yield of ketone was lower.

Indan, 1,2,3,4-tetrahydronaphthalene and 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene (Tables 12 and 13). Two independent experiments were performed (ceric triflate to arene 2:1). The indan-1-one and indan-1-ol were both observed,

Table 5 Oxidation of diphenylmethane



Table 6 Oxidation of bibenzyl





Substrate	Time	% $H_2O$ in Ce(OTf) <sub>4</sub>	Ce(OTf) <sub>4</sub> /mmol	Substrate/mmol	Product yiel	Product yield (%)	
 2	3 h	16.06	0.680	0.340	2a (70.8)	<b>2b</b> (23.3)	
3	25 h	22.0	0.700	0.350	3a (—)	<b>3b</b> (100)	
3	22 h	22.0	$0.640^{a}$	$0.320^{a}$	<b>3a</b> $(100)^a$	_ `	
4	75 h	16.06	0.670	0.335	4a (25.6)	<b>4b</b> (52.4)	
4	20 min		0.570	0.285	<b>4a</b> (18.2)	<b>4b</b> (5.2)	
5	28 h	11.10	0.700	0.345	5a (—)	5b (—)	
5	4 h	_	0.560	0.280	<b>5a</b> (16.5)	5b (—)	

<sup>a</sup> 4-Fluorobenzyl alcohol obtained from the previous reaction was treated with a second equivalent of Ce(OTf)<sub>4</sub>.



<sup>a</sup> Products were identified via <sup>1</sup>H NMR analysis.

#### Table 8 Oxidation of o-ethyltoluene



#### Table 9 Oxidation of p-diethylbenzene



Tima/	% H <sub>2</sub> O in Ce(OTf) <sub>4</sub>	Ce(OTf) <sub>4</sub> / mmol	Substrate/ mmol	%Yield			
h				10a	10b	10c	10d
24 22	14.5 16.4	0.626 0.700	0.313 0.350	$23.0^{a}$ $45.6^{a}$	$17.2^{a}$ 27.8 <sup>a</sup>	$55.5^{a}$ $6.5^{a}$	$4.3^{a}$ 17.6 <sup>a</sup>
25	22.0	$1.400^{b}$	0.350	61.3	33.3	3.6	_

<sup>*a*</sup> Products were identified *via* <sup>1</sup>H NMR analysis. <sup>*b*</sup> Stepwise addition of 2 equivalents of Ce(OTf)<sub>4</sub>, second 2 equivalents were added after 2 hours stirring.

with the ketone being the predominant product. Under these conditions the yield of indanone was around 48%. Tetrahydronaphthalene was similarly oxidized to give the benzylic ketone Table 10 Oxidation of *m*-diethylbenzene



#### Table 11 Oxidation of *n*-butylbenzene



Table 12 Oxidation of indan



and the alcohol depending on the % H<sub>2</sub>O present in ceric triflate. Surprisingly 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene was not oxidized.

**9,10-Dihydrophenanthrene and 1-methylnaphthalene (Tables 14 and 15).** With dihydrophenanthrene both mono- and dioxo compounds were formed with the diketone predominating. 1-Methylnaphthalene was oxidized to the aldehyde in modest yields and no alcohol could be detected.

Methoxyalkylbenzenes (alkylanisoles) (Table 16). 4-Ethylanisole was oxidized in reasonable yields to give a mixture of ketone and alcohol with the ketone dominating. Under similar conditions 2-methylanisole was not oxidized with ceric triflate.



Table 14 Oxidation of 9,10-dihydrophenanthrene



Table 15 Oxidation of 1-methylnaphthalene



**Bromomesitylene and hexamethylbenzene.** With bromomesitylene, the monoaldehyde, the alcohol and the dialdehyde were produced upon reaction with ceric triflate, but the conversion was modest (28% total). Hexamethylbenzene was recovered intact (<sup>1</sup>H NMR).

4-Nitrotoluene, 4,4'-dimethylbiphenyl and [2.2]paracyclophane. In two independent reactions, cerium triflate oxidation of 4-nitrotoluene gave only traces of 4-nitrotolualdehyde. The CAN-promoted oxidation of this compound in hot HClO<sub>4</sub> was reported to give 47% conversion.<sup>1</sup> The 4,4'-dimethylbiphenyl produced <1% of the monoaldehyde and [2.2]paracyclophane gave only a trace of [2.2]paracyclophan-1-one. 
 Table 16
 Oxidation of p-ethylanisole



## Color changes accompanying ceric triflate oxidation

Addition of ceric triflate to EtPh in MeCN solvent initially generates a clear yellow solution which after 3 minutes changes into orange with a white suspension. After about one hour stirring at rt, the reaction mixture changes into a bleached-white suspension which does not change further with time. Similar color variations were noted with ethyltoluene isomers, diethylbenzene isomers, and halotoluene isomers studied. The more electron rich arenes appear to undergo a more rapid color change leading to the white suspension. With indan, the color is initially orange and subsequently white. With tetrahydronaphthalene it changes from yellow to white, with diphenylmethane it goes from orange to a white–orange suspension; those of 1-methylnaphthalene and tetrahydrophenanthrene change from yellow to black and alkylanisoles from clear yellow to blue– purple.

#### Comments on the mechanism

Based on several early mechanistic studies, it can be surmised that benzylic oxidation mediated by CAN involves initial electron transfer to form a radical cation, followed by  $\alpha$ -proton loss to form a benzylic radical whose oxidation gives a benzylic carbocation.<sup>9</sup> With CAN, side chain nitration could stem from nucelophilic quenching by nitrate ligand which depending on the relative stability of the carbocation competes with solvent capture.<sup>9a</sup> Additional studies revealed that nitration but not side-chain substitution can be suppressed by addition of water. It was suggested that a cerium complex is formed from which nitronium ion is produced which then nitrates the arene.<sup>9b</sup> With cerium trifluoroacetate, the arene radical cation reacts to produce biaryls, diarylmethanes and the trifluoroacetate ester.<sup>11</sup>

In line with these studies, the initial step of  $Ce(OTf)_4$  oxidation is most likely a charge transfer complex which is followed by electron transfer to the radical cation. Similar steps as proposed with CAN oxidation can be envisioned leading to the benzylic carbocation, which is quenched with water to give the alcohol whose further oxidation gives the benzylic carbonyl compounds. As mentioned earlier, conversion to the carbonyl compound is initially quite rapid as no alcohol was detected. But prolonged reaction times produce the alcohol *via* a slow oxidation of the unreacted arene and this is likely induced by Ce(III) triflate.

A link has been established between the % H<sub>2</sub>O in ceric triflate and oxidation ability and an optimal range for effective oxidation has been defined. The fact that significant amounts of benzylic alcohol are formed from the more anhydrous ceric triflate samples implies that oxidation ability (leading eventually to benzylic carbocation) has in fact diminished, otherwise, these samples should have produced less alcohol and possibly led to biaryls, diphenylmethanes and even benzylic triflates. However, these side products were never observed, which also illustrates that ceric triflate has superior chemoselectivity towards benzylic oxidation as compared to CAN or ceric trifluoroacetate. In oxidation reactions with ethyltoluenes there is a strong preference for benzylic methylene oxidation as compared to benzylic methyl oxidation.

Samples purchased commercially exhibited low oxidation power. Attempts to activate them by adjusting the %  $H_2O$  to "optimal level" were only partially successful since only benzylic alcohol (not the ketone) could be produced in high yield. By comparison, ceric triflate does not perform well for nitroarenes in rt reactions, however, on the whole, cerium triflate appears to exhibit a broader substrate tolerance than CAN. A noteworthy feature of the present work is the ease of operation in room temperature oxidaton reactions requiring no special equipment or precaution, provided Ce(OTf)<sub>4</sub> is correctly prepared and the water content is kept in the optimal range.

### Experimental

#### Starting materials

Triflic acid (Aldrich) was distilled under a dry nitrogen atmosphere in an all-glass distillation unit and stored in a Nalgene bottle with a Teflon seal. 1,1,2-Trichlorotrifluoroethane (Freon-113), CAN and cerium trifluoromethanesulfonate ( $2 \times 1$  g samples) were purchased from Aldrich and used as received.

#### Preparation of cerium(IV) triflate

(Method 1). A solution of potassium carbonate (4.24 g, 30.6 mmol) in distilled water (24 mL) was added all at once to a vigorously stirred solution of cerium ammonium nitrate (CAN) (7.00 g, 12.8 mmol) in distilled water (21 mL) whereby the initial clear orange solution formed a pale-yellow precipitate (gas evolution). After 30 min stirring at rt the precipitate was collected by filtration and washed thoroughly with water (350 mL) to remove excess potassium carbonate. The resulting moist ceric carbonate was transferred into a 500 mL round-bottom flask equipped with a magentic stirrer bar and a septum. The flask was cooled in an ice-bath and triflic acid (4.52 mL, 51.1 mmol) was added dropwise via a syringe over a 30 minute period (CO<sub>2</sub> evolution was observed). After stirring for an additional 1 h, the resulting clear orange solution was evaporated under reduced pressure to afford a yellow residue which was dried in a vacuum desiccator to yield a canary-yellow solid. Typical yields in independent preparations: 8.21 g (88%; 16.06% H<sub>2</sub>O from TGA exp.); 10.02 g (92%; 14.4% H<sub>2</sub>O from TGA exp.).

(Method 2). The above procedure was followed up to isolation of cerium carbonate and its transfer into the roundbottom flask. After cooling (ice-bath), Freon-113 (25 mL) was first added followed by triflic acid (4.52 mL, 51.1. mmol). After 1 h, the resulting clear orange solution was evaporated under reduced pressure to afford a yellow residue which was then dried as before to furnish a light-yellow solid. Typical yields in independent preparations: 9.98 g (93%; 12.8% H<sub>2</sub>O); 9.42 g (78%, 14% H<sub>2</sub>O); 10.82 (90%, 22% H<sub>2</sub>O), 10.21 g (91%; 16.4% H<sub>2</sub>O); Among various batches synthesized by this method there was a sample whose H<sub>2</sub>O content was estimated as 1.5%.

#### General procedure for arene oxidation

Ceric triflate (2 equivalents; ~0.680 mmol) was added all at once to a vigorously stirred solution of the arene substrate in dry MeCN (10 mL) at rt, initially resulting in a clear yellow (or orange) solution depending on the substrate. Upon stirring, color changes are observed depending on the substrate (see Discussion). After the indicated reaction time (see tables) the mixture was poured into a separatory funnel along with distilled water (2 × 15 mL). The organic layer was extracted into  $CH_2Cl_2$  (2 × 15 mL), washed with water (2 × 15 mL) and dried (MgSO<sub>4</sub> s). After filtration, the solvent was gently removed under vacuum and the residue was analyzed by GC. The oxidation products were all known compounds whose identities were established by coinjection with authentic samples, by GC-MS and in selected cases by isolation and NMR analysis.

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