## SELECTIVE OXIDATIONS WITH CERIC METHANESULFONATE AND CERIC TRIFLUOROMETHANESULFONATE

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Summary. Cerium(IV) in aqueous methanesulfonic acid and trifluoromethanesulfonic acid are excellent reagents for the oxidation of alkyl and polycyclic aromatics to aromatic aldehydes, ketones and quinones.

The ceric ion has been known for some time to be a selective oxidizing agent in the synthesis of aromatic aldehydes and ketones from alkyl aromatics and quinones from polycyclic aromatics.<sup>1,2</sup> However, the anions used with cerium(IV) have greatly limited its usefulness due to instability toward oxidation (e.g., chloride<sup>3</sup>), undesired reactivity with the organic substrates (e.g., nitrate, <sup>1,4</sup> chloride,<sup>3</sup>, perchlorate<sup>5</sup>) or marginal solubility and slow organic oxidations (e.g., sulfate,  $^{6,7}$  acetate,  $^{8}$  trifluoroacetate<sup>9</sup>). We have found that cerium salts of methanesulfonate and trifluoromethanesulfonate obviate the above problems, give high selectivities for a wide range of substrates (Table I) and are easily recycled by electrochemical oxidation with high efficiency at high current densities. Also, the organic oxidations are fast under conditions where the cerium salts are soluble and the organic products are immiscible with the aqueous solutions, making for facile product separation. In these respects, ceric methanesulfonate and ceric trifluoromethanesulfonate are clearly superior to Cr(VI), <sup>10</sup> Mn(III), <sup>11</sup> other known Ce(IV) reagents 1-7,9 and direct electrochemical oxidation. 12

Substrate	Conc. CH <sub>3</sub> SO <sub>3</sub> H(M)	Temp. (°C)	Reaction Time (min)	Products	Yield Based on Substrate
toluene	5.5	80	10	benzaldehyde	91
toluene	2.4 <sup>a</sup>	25	40	benzaldehyde	75
m-xylene	5.5	60	10	m-tolualdehyde	70
p-chlorotoluene	5.5	80	15	p-chlorobenzaldehyde	e 86
ethylbenzene	5.5	80	13	acetophenone	44
naphthalene <sup>b</sup>	2.5	60	35	1,4-naphthoquinone	89
anthracene <sup>b</sup>	5.0	25	4	9,10-anthraquinone	95
p-methylanisole <sup>C</sup>	3.6	5	40	p-anisaldehyde	71

Table I. Oxidations with Ce(IV) in Methanesulfonic Acid and Trifluoromethanesulfonic Acid

<sup>a</sup>CF<sub>3</sub>SO<sub>3</sub>H used in place of CH<sub>3</sub>SO<sub>3</sub>H. <sup>b</sup>Substrate diluted 1:20 with 1,2-dichloroethane before addition. <sup>C</sup>Aqueous solution diluted 1:2 with methanol prior to substrate addition.<sup>13</sup>

Preparation of Cerium(IV) Solutions: To a stirred suspension of 53g of cerous carbonate in 160 ml of water, 240g of methanesulfonic acid was added dropwise, with CO<sub>2</sub> evolution, resulting in 0.6M cerous methanesulfonate  $(Ce(CH_2SO_2)_2 \cdot 2H_2O)^{14}$  and 6M methanesulfonic acid. This solution (320 ml) was introduced into the anolyte compartment of a plate and frame type electrolytic cell.<sup>15</sup> The anode was platinum-clad niobium expanded mesh having both surfaces coated with 63.5 micrometers of platinum (total surface area of ca. 240  $\text{cm}^2$ ). The anolyte was separated from the catholyte (6M CH<sub>3</sub>SO<sub>3</sub>H) by a commercial perfluorinated ion exchange membrane (Nafion 390) (area=50  $cm^2$ ) and was heated at 50°C while a constant current of 14 amps was passed for 22 minutes. The resultant orange solution had a Ce(IV) concentration of 0.53 molar (current efficiency=88%). The catholyte compartment contained a stainless steel cathode and caused a clean reduction of protons to hydrogen The preparation of Ce(IV) in aqueous trifluoromethanesulfonic acid was gas. analogous to the above. General Oxidation Procedure: The above solution (320 ml) from the electrolytic cell was stirred vigorously at 80°C under a nitrogen atmosphere. Toluene(2.77 g, 0.03 moles) was added and stirring was continued for 10 minutes. The resultant colorless mixture was extracted with 3 x 170 ml of methylene chloride. The combined extracts were dried (MgSO,) and analyzed quantitatively by gas chromatography (dodecane internal standard) showing 98.5% conversion of toluene and 92% selectivity to benzaldehyde. The Ce(III) solution was re-electrolyzed with results identical to those described above. Acknowledgement: We thank G. W. Ambrose-Ritchey, J. B. Davis, W. L. Henry, V. R. Hoover and D. S. McFarland for technical assistance. References

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