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Cerium(IV) Trifluoromethanesulfonate as a Strong Oxidizing Agent

Tsuneo IMAMOTO,* Yasuhiro KOIDE, and Susumu HIYAMA*†
Department of Chemistry, Faculty of Science, Chiba University,
Yayoi-cho, Chiba 260
†Seimi Chemical Co. Ltd., Chigasaki, Kanagawa 253

Cerium(IV) trifluoromethanesulfonate was prepared by the reaction of cerium(IV) carbonate with trifluoromethanesulfonic acid. The powerful oxidizing ability of this compound is observed in the oxidation of benzyl alcohols and alkylbenzenes.

Recently, Kreh et al. reported that cerium(IV) trifluoromethanesulfonate was generated in situ in aqueous trifluoromethanesulfonic acid by an electrochemical method.[1,2] However, the isolation of this compound has not yet been reported, despite its anticipated synthetic utility as a very strong oxidizing agent.

We have succeeded in preparing this tetravalent cerium salt by the reaction of cerium(IV) carbonate with trifluoromethanesulfonic acid. This communication deals with the first isolation of this compound and its high oxidizing ability toward some organic compounds.

Cerium(IV) trifluoromethanesulfonate was prepared in the following manner. A solution of potassium carbonate (17.3 g, 0.12 mol) in 95 ml of water was added with vigorous stirring to a solution of cerium(IV) ammonium nitrate (CAN) (27.4 g, 0.05 mol) in 80 ml of water, whereupon a pale yellow precipitate was produced. This precipitate was collected by filtration and washed with water several times. Trifluoromethanesulfonic acid (17.7 ml, 0.2 mol) was slowly added at 0 °C to the wet cerium(IV) carbonate prepared above.[3,4] The resulting orange-colored solution was evaporated under reduced pressure, and the residue was dried in vacuo at 70 °C for 10 h to give yellow powder (36.2 g).[5,6]

$$(NH_4)_2Ce(NO_3)_6 \xrightarrow[2)\ 4\ CF_3SO_3H]{1)\ 2\ K_2CO_3} Ce(OSO_2CF_3)_4$$

The oxidizing ability of cerium(IV) trifluoromethanesulfonate was examined by the use of benzyl alcohols and alkylbenzenes as model substrates. The reactions were carried out at room temperature. Some representative results are shown in Table 1. *p*-Chlorobenzyl alcohol was rapidly oxidized to the corresponding aldehyde in high yield; no trace of *p*-chlorobenzoic acid was produced under these conditions. 1,2-Bis(*p*-chlorophenyl)-1,2-ethanediol was subjected to an oxidative carbon-carbon bond cleavage to *p*-chlorobenzaldehyde. *p*-Bromotoluene and *o*-xylene were selectively converted to *p*-bromobenzaldehyde and *o*-tolualdehyde, respectively. These results are in contrast to the oxidation with CAN which is often accompanied by undesirable side reactions.[7] Although the data are limited, we believe that cerium(IV) trifluoromethanesulfonate has potential synthetic utility as a strong and selective oxidant.

Table1. Oxidation of Benzyl Alcohols and Alkylbenzenes with $Ce(OTf)_4$ [a,b]

Substrate	Molar ratio $Ce(OTf)_4$: Substrate	Time h	Product	Yield[c] %
p-$ClC_6H_4CH_2OH$	2.5	1	p-ClC_6H_4CHO	92
p-$MeOC_6H_4CH_2OH$ [d]	2.5	0.5	p-$MeOC_6H_4CHO$	72
p-$O_2NC_6H_4CH_2OH$ [e]	2.5	1	p-$O_2NC_6H_4CHO$	84
$C_6H_5CH(OH)CH_3$	2.5	1.5	$C_6H_5COCH_3$	76
$[p$-$ClC_6H_4CH(OH)]_2$ [f]	2.5	1	p-ClC_6H_4CHO	68
p-$BrC_6H_4CH_3$	4.5	2.5	p-BrC_6H_4CHO	58
o-$MeC_6H_4CH_3$	4.5	1.5	o-MeC_6H_4CHO	70
$C_6H_5CH_2CH_3$	4.5	2	$C_6H_5COCH_3$	65
$C_6H_5CH_2C_6H_5$	4.5	3	$C_6H_5COC_6H_5$	68

a) All reactions were carried out in MeCN-H_2O (1:1) unless otherwise stated. b) $Ce(OTf)_4 = Ce(OSO_2CF_3)_4$. c) Isolated yield. d) In MeOH-H_2O (1:1). e) The reaction was carried out in the presence of 10 equiv. of CF_3SO_3H. f) In MeCN-H_2O (2:1).

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References

1) R. P. Kreh, R. M. Spontiz, and J. T. Lundquist, *Tetrahedron Lett.*, **28**, 1067 (1987).

2) Kreh et al. prepared cerium(IV) methanesulfonate by the same method, and they indicated that this compound also exihibited strong oxidizing ability. R. P. Kreh, R. M. Spontiz, and J. T. Lundquist, *J. Org. Chem.*, **54**, 1526 (1989).

3) An attempt to prepare cerium(IV) trifluoromethanesulfonate by the reaction of cerium(IV) hydroxide or cerium(IV) oxide with trifluoromethanesulfonic acid was unsuccessful.

4) Use of "wet" cerium(IV) carbonate is essential. Dry cerium(IV) carbonate did not react with trifluoromethanesulfonic acid at 0 °C.

5) IR(KBr): 1230 ($\nu_{S=O}$),1010 cm^{-1} (ν_{C-F}). Found : C, 6.29; H, 0.54; Ce, 18.37; F, 31.20; S, 16.02; H_2O (Karl Fischer), 3.70%. Calcd for $C_4H_4F_{12}O_{12}S_4Ce$ $1.5H_2O$: C, 6.29; H, 0.40; Ce, 18.35; F, 29.86; S, 16.80; H_2O, 3.54%.

6) This compound is hygroscopic and is soluble in water, ethanol, tetrahydrofuran, 1,2-dimethoxyethane, and dioxane; it is practically insoluble in dichloromethane, hexane, and benzene. It gradually decomposes above 120 °C to give a trivalent cerium species.

7) E. Baciocci, C. Rol, G. V. Sebastiani, and B. Serena, *Tetrahedron Lett.*, **25**, 1945 (1984); S. Dincturk and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 961; H. B. Kagan, *Tetrahedron*, **42**, 6573 (1986) and references cited therein.

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