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# Preparative Conversion of Oximes to Parent Carbonyl Compounds by Cerium(IV) Sulfate in Acetonitrile and Alcohol

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**A new method for the direct conversion of oximes into aldehydes and ketones by treatment with cerium(IV) salts is described. Cerium(IV) salts can be used as an effective and mild oxidizing agent for the regeneration of carbonyl compounds from oximes in good yield. The solvent effects are discussed. Copyright © 1999 John Wiley & Sons, Ltd.**

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## INTRODUCTION

Cerium(IV) salts as an oxidant have attracted considerable attention recently.[1] Their power as oxidants is evident from the fact that the standard redox potential of Ce(IV)–Ce(III) is approximately 1.6 V. We have investigated novel iodination methods using iodine–cerium(IV) ammonium nitrate (CAN) or iodine–cerium(IV) sulfate (CS) and reported some new reactions: a novel $\alpha$-iodination of ketones in acetic acid or methanol;[2,3] new alkoxyiodinations and nitratoiodinations of olefins,[4] $\alpha$, $\beta$-unsaturated ketones and esters;[5] and a new $\alpha$, $\alpha'$-diiodination of ketones.[6] Throughout our studies, many interesting results of the reactions with $I_2$–CAN and $I_2$–CS have been observed in a wide variety of organic substrates.

Oximes of carbonyl compounds are important because of their use in purification and characterization of parent carbonyl compounds, and in synthesis. A variety of methods have been developed for the oxidative cleavage of oximes and semicarbazones.[7–21] Ion-exchange resins[22,23] have also been found to be superior for the regeneration of carbonyl compounds from their nitrogenous derivatives. Although these methods are generally useful, only a limited number of methods are available for this conversion under mild reaction conditions. In this paper, we describe a new method for the direct conversion of oximes into aldehydes and ketones by treatment with cerium(IV) salts in acetonitrile and alcohols (Scheme 1).

The reaction of ketone and aldehyde oximes with cerium(IV) salts in acetonitrile and alcohols readily yields the parent carbonyl compounds. The reaction of each of the oximes with cerium (IV) sulfate tetrahydrate (CS) in acetonitrile at 50 °C for 3–4 h gave the parent carbonyl compounds in excellent yields. These results are summarized in Table 1, which shows that the reaction proved to be general in the preparative conversion of oximes to parent carbonyl compounds by CS in acetonitrile. However, in the case of tetraammonium cerium(IV) sulfate dihydrate (CAS), because of its weak oxidative properties and poor solubility in MeCN, the yield of the conversion reaction is low under the same reaction conditions. Solid compounds were formed in the reaction process by using CAN in MeCN, and parent carbonyl compounds were not obtained.

We also developed the reactions of cycloalkanone oximes and 2-alkylcycloalkanone oximes with CAN, CAS and CS in alcohols of methanol, ethanol and propanol. With CAN the reaction is faster than that with CAS or CS, because CAN can be completely dissolved in MeOH. In the case of the oximes of 2-alkylcycloalkanones (run 13) and cyclopentanone (run 1), however, oxidative ring-cleavage reactions occurred when using CAN in MeOH because the oxidative capacity of CAN is stronger than that of CS in MeOH. In the case of CAN, CAS and CS in ethanol or propanol, the parent ketone compounds were also obtained in

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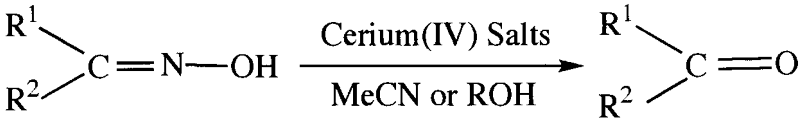

**Scheme 1** $R^1$ = alkyl, $R^2$ = alkyl or H.

good yield. For seven-, eight- and twelve-membered rings, the parent ketone compounds were formed in excellent yields (runs 21, 23 and 25).

From an examination of the reactions of a wide range of oximes with cerium(IV) salts under a variety of conditions, the advantages of the present method can be summarized as follows: (1) reaction proceeds on the free oximes; (2) although 2-

**Table 1** Deprotection reactions of carbonyl compound oximes with Ce(IV) salts in MeCN and alcohols[a]

| Run | Oxime | Cerium(IV) salt | Solvent | *t* (h) | Yield of carbonyl compound (%)[b],[c] |
|---|---|---|---|---|---|
| 1[d] | Cyclopentanone | CAN | MeOH | 1 min | 54 |
| 2 | | CAS | MeCN | 3 | 17 |
| 3 | | CS | MeCN | 3 | 95 |
| 4 | | CS | MeOH | 4 | 80 |
| 5 | | CS | EtOH | 10 | 90 |
| 6 | 2-Methylcyclopentanone | CAS | MeCN | 4 | 28 |
| 7 | | CS | MeCN | 4 | 89 |
| 8 | | CS | MeOH | 4 | 88 |
| 9 | Cyclohexanone | CAS | MeCN | 4 | 53 |
| 10 | | CS | MeCN | 4 | 91 |
| 11 | | CAN | MeOH | 1 min | 89 |
| 12 | | CS | MeOH | 4 | 90 |
| 13[e] | 2-Methylcyclohexanone | CAN | MeOH | 3 min | 45 |
| 14 | | CAS | MeCN | 4 | 30 |
| 15 | | CS | MeCN | 4 | 87 |
| 16 | | CS | MeOH | 6 | 87 |
| 17 | 2,5-Dimethylcyclohexanone | CAS | MeCN | 4 | 24 |
| 18 | | CS | MeCN | 3 | 94 |
| 19 | 2-Propylcyclohexanone | CS | MeCN | 4 | 88 |
| 20 | Menthone | CS | MeCN | 4 | 91 |
| 21 | Cycloheptanone | CS | MeCN | 4 | 91 |
| 22 | | CS | MeOH | 6 | 90 |
| 23 | Cyclooctanone | CS | MeCN | 4 | 92 |
| 24 | | CS | MeOH | 6 | 91 |
| 25 | Cyclododecanone | CS | MeCN | 4 | 92 |
| 26 | | CS | MeOH | 6 | 93 |
| 27 | Pentan-2-one | CS | MeCN | 3 | 78 |
| 28 | Pentan-2-one | CS | MeCN | 3 | 81 |
| 29 | 5-Hexen-2-one | CS | MeCN | 3 | 91 |
| 30 | Benzaldehyde | CS | MeCN | 3 | 94 |
| 31 | *m*-Tolualdehyde | CS | MeCN | 3 | 81 |
| 32 | 5*α*-Cholestan-3-one | CS | MeCN | 4 | 96 |
| 33 | 5*β*-Cholestan-3-one | CS | MeCN | 4 | 93 |

[a] Reaction conditions: Substrate (2.0 mmol), Ce(IV) salt (4.0 mmol) and solvent (25 ml) were employed under an oxygen atmosphere ($O_2$-balloon) at 50 °C (room temp. for CAN).
[b] Isolated yield.
[c] The regenerated carbonyl compounds were checked by comparison (IR, $^1$H NMR and $^{13}$C NMR spectra) with authentic samples.
[d] Ring oxidative cleavage compound was obtained in 35% yield.
[e] Methyl 6-oxoheptanoate was obtained in 41% yield.

alkylcycloalkanone oximes can be oxidatively cleaved by CS in alcohols, under these reaction conditions ketone oximes in acetonitrile and alcohols readily yield the parent carbonyl compounds in good yields.

In this reaction, cerium(IV) salts would act as an oxidizing agent toward oximes but not as a hydrolyzing agent, similarly to lead tetraacetate oxidation.[24]

## EXPERIMENTAL

### General

IR spectra were measured using a Jasco FT-IR 230 spectrometer. NMR spectra were measured on a JOEL GSX 400 spectrometer with the samples dissolved in deuteriochloroform with tetramethylsilane (TMS) as an internal standand. High-resolution mass spectra were recorded at 75 eV on a JEOL JMS-O1SG-2 instrument with a direct inlet.

### Typical procedures

**Reaction of 2-methylcyclohexanone oxime with CS in MeCN**

A mixture of 2-methylcyclohexanone oxime (0.254 g, 2.00 mmol) and cerium(IV) sulfate tetrahydrate (1.617 g, 4.00 mmol) in MeCN (25 ml) was stirred at 50 °C under an oxygen atmosphere for 4 h. The white precipitate was filtered off and the reaction solvent was removed under reduced pressure. The residue was poured into water (20 ml) and extracted with diethyl ether ($2 \times 25$ ml). The ethereal solution was washed successively with a saturated aqueous solution of NaCl (10 ml), aqueous sodium hydrogencarbonate ($NaHCO_3$) solution (10 ml) and water (10 ml), dried with $Na_2SO_4$ and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–ether (3:1) gave 2-methylcyclohexanone as a colorless oil (0.195 g, 87%).

**Reaction of 2-methylcyclohexanone oxime with CS in MeOH**

A mixture of 2-methyclcyclohexanone oxime (0.254 g, 2.0 mmol) and cerium (IV) sulfate tetrahydrate (1.616 g, 4.0 mmol) in MeOH (25 ml) was stirred at 50 °C under an oxygen atmosphere for 6 h. Filtration, extraction, washing, concentration and chromatography as described above gave 2-methylcyclohexanone as a colorless oil (0.197 g, 87%).

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## REFERENCES

1. G. A. Molander, *Chem. Rev.* **92**, 29 (1992).
2. C. A. Horiuchi and S. Kiji, *Chem. Lett.* 31 (1988).
3. C. A. Horiuchi and S. Kiji, *Bull. Chem. Soc. Jpn.* **70**, 421 (1997).
4. C. A. Horiuchi, K. Ochiai and H. Fukunishi, *Chem. Lett.* 185 (1994).
5. C. A. Horiuchi, H. Fukunishi, M. Kajita, A. Yamaguchi, H. Kiyomiya and S. Kiji, *Chem. Lett.* 1921 (1991).
6. C. A. Horiuchi and E. Takahashi, *Bull. Chem. Soc. Jpn.* **67**, 271 (1994).
7. A. S. Demir, C. Tanyeli and E. Altinel, *Tetrahedron Lett.* **38**, 7267 (1997).
8. N. B. Barhate, A. S. Gajire, R. D. Wakharkar and A. Sudalai, *Tetrahedron Lett.* **38**, 653 (1997).
9. M. Curini, O. Rosati and E. Pisani, *Synlett* 333 (1996).
10. T. Shinada and K. Yoshihara, *Tetrahedron Lett.* **36**, 6701 (1995).
11. A. McKillop, J. D. Hunt, R. D. Naylor and E. C. Taylor, *J. Am. Chem. Soc.* **93**, 4918 (1971).
12. J. G. Lee, K. H. Kwak and J. B. Hwang, *Tetrahedron Lett.* **31**, 6677 (1990).
13. D. P. Curran, J. F. Brill and P. D. Rakiewics, *J. Org. Chem.* **49**, 1654 (1984).
14. P. Larzlo and E. Polla, *Synthesis* 439 (1985).
15. G. A. Olah, Q. Liao, C. S. Lee and G. K. Surayaprakash, *Synlett* 427 (1993).
16. R. Joseph, A. Sudalai and T. Ravindranathan, *Tetrahedron Lett.* **35**, 5493 (1994).
17. P. Kumar, V. R. Hedge, B. Padney and T. Ravindranathan, *J. Chem. Soc., Chem. Commun.* 1553 (1993).
18. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Perkin Trans.* **1** 1212 (1980).
19. P. Vankar, R. Rathore and S. Chandrasekaran, *J. Org. Chem.* **51**, 3063 (1986).
20. J. W. Bird and D. G. M. Diaper, *Can. J. Chem.* **47**, 145 (1969).
21. G.-S. Zhang, D.-H. Yang, M.-F. Chen and K. Cai, *Synth. Commun.* **28**, 2221 (1998).
22. B. C. Ranu and D. C. Sarkar, *J. Org. Chem.* **53**, 878 (1988).
23. R. Ballini and M. Petrini, *J. Chem. Soc., Perkin Trans. 1* 2563 (1988).
24. Y. Yukawa, M. Sakai and S. Suzuki, *Bull. Chem. Soc. Jpn.* **39**, 2266 (1966).