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Reaction of olefins using cerium(IV) sulfate tetrahydrate in carbonyl compounds–H_2O

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The reaction of olefins with cerium(IV) sulfate tetrahydrate [$Ce(SO_4)_2 \cdot 4H_2O$, CS] in acetone–H_2O under reflux for 5 h gave 2-oxo- and 2-oxo-5-hydroxy derivatives. In this reaction, the yields of 2-oxo-5-hydroxy derivatives were dependent on the quantity of H_2O. Moreover, the reaction of α, β-unsaturated ketones with CS in acetone–H_2O yielded 2,7-dioxo-3-hydroxy or 3,8-dioxo-4-hydroxy derivatives. The reaction mechanism is also discussed. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: alkenes; ketones; additions; cerium(IV) sulfate tetrahydrate; H_2O

INTRODUCTION

In synthetic chemistry, addition reactions including formation of a carbon–carbon bond by a radical species have been studied because of their peculiar reactivity.[1] It is known that the formation of carbon–carbon bonds using radical species by one-electron oxidation is used as a self-coupling reaction.[2–4] A few examples of intermolecular carbon–carbon bond formation have been reported.[5,6] Recently, we found several novel reactions using cerium(IV) salts: α-iodination of ketones in acetic acid or alcohols,[7] alkoxyiodination and nitratoiodination of olefins and α,β-unsaturated esters,[8] α,α'-diiodination of ketones using iodine–ammonium cerium(IV) nitrate (CAN(IV)),[9] and a novel one-pot synthesis of 3-acetyl- and 3-benzoylisoxazole derivatives using CAN.[10,11] More recently, we reported that the reaction of cycloalkanone, 2-alkylcycloalkanone, and 2-halocycloalkanone with cerium(IV) sulfate tetrahydrate (CS) in alcohols and acetic acid yields the corresponding esters of oxo acids, diesters, oxo acids, and dionic acids.[12]

In this paper, we report the reaction of olefins with CS in acetone–H_2O under reflux for 5 h to give 2-oxo derivatives as major products and 2-oxo-5-hydroxy derivatives as by-products. In the case of 2-butanone or 3-pentanone, the corresponding 2-oxo-3-methyl-, 3-oxo- or 3-oxo-4-methyl derivatives are obtained. This is an intermolecular C–C bond forming reaction, and a new synthetic route to 2-oxo-5-hydroxy derivatives. Furthermore, it was found that the yields of 2-oxo-5-hydroxy derivatives depend on the H_2O concentration. The reaction of α,β-unsaturated ketones with CS in acetone–H_2O yielded 2,7-dioxo-3-hydroxy or 3,8-dioxo-4-hydroxy derivatives. The reaction mechanism appears to be based on an addition reaction that forms of new carbon–carbon bonds.

EXPERIMENTAL

General

IR spectra were recorded on a Jasco FT-IR 230 spectrometer. Both ^1H and ^{13}C NMR spectra were measured on a Jeol GSX-400 spectrometer (400 MHz for ^1H; 100 MHz for ^{13}C). Chemical shifts were reported on the δ scale (ppm) with solvent ($CHCl_3 = 7.26$) as an internal standard. The signal of the solvent ($CDCl_3 = 77.00$) was used as a standard for ^{13}C NMR spectra. Both low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on a Shimadzu GCMS-QP5050 and JMS-GCMATE II mass spectrometer with the chemical ionization (CI) method unless noted otherwise. Analytical thin-layer chromatography (TLC) was done on precoated TLC plates (silica gel 60 F254, layer thickness 0.2 mm). Silica gel 60 (0.063–0.200 mm) was used for column chromatography. All chemicals were purchased from Kanto Kagaku, Tokyo Kasei Kogyo Corporation and Wako Pure Chemical Industries, Ltd.

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Reaction of 1-octene (3) with CS in acetone–H_2O

A mixture of 1-octene (**3**) (0.2244 g, 2.0 mmol) and CS (0.8086 g, 2.0 mmol) in acetone (10.5 ml)–H_2O (1.5 ml) was stirred under reflux for 5 h. The reaction mixture was extracted with diethyl ether (30 ml) and washed with aqueous sodium bicarbonate solution (2 × 2.0 ml), saturated aqueous NaCl (2 × 2.0 ml), and water (2 × 2.0 ml). The ethereal solution was dried over Na_2SO_4 and concentrated in a vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–diethyl ether (4 : 1) gave 2-undecanone (**3a**: 0.2837 g, 84%) and 5-hydroxy-2-undecanone (**3b**: 0.0505 g, 14 %).

*5-Hydroxy-2-pentadecanone (**5b**)*

Pale-yellow oil; IR (NaCl) 3423 and 1716 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 4.14$ (m, 1H), 3.56 (brs, 1H), 2.61 (t, 2H), 2.17 (s, 3H), 1.17–1.45 (m, 18H), and 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$) $\delta = 209.7$, 71.5, 40.1, 38.6, 37.8, 35.8, 31.9, 30.9, 30.0, 29.7, 29.6, 29.5, 29.4, 25.7, and 22.7. HRMS Found: m/z 224.2135 $[M - H_2O]^+$. Calc. for $C_{15}H_{28}O$: M, 224.2140.

Reaction of 1-hexene (1) and 2-butanone with CS in methanol–H_2O

A mixture of 1-hexene (**1**) (0.1683 g, 2.0 mmol), CS (0.1617 g, 0.4 mmol) and 2-butanone (7.0 ml) in methanol (4.0 ml)–H_2O (1.0 ml) was stirred under reflux for 5 h. The reaction mixture was extracted with diethyl ether (30 ml) and washed with aqueous sodium hydrogencarbonate solution (2 × 2.0 ml), saturated aqueous NaCl (2 × 2.0 ml), and water (2 × 2.0 ml). The ethereal solution was dried over Na_2SO_4 and concentrated in a vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–diethyl ether (4 : 1) gave 3-methyl-2-nonanone (**1c**: 0.0343 g, 11%) and 3-decanone (**1d**: 0.0031 g, 1%).

Reaction of 1-buten-3-one (6) with CS in acetone–H_2O

A mixture of 1-buten-3-one (**6**) (0.2103 g, 3.0 mmol) and CS (0.1213 g, 0.3 mmol) in acetone (10.0 ml)–H_2O (1.0 ml) was stirred under reflux for 1 h. The reaction mixture was extracted with diethyl ether (30 ml) and washed with aqueous sodium bicarbonate solution (2 × 2.0 ml), saturated aqueous NaCl (2 × 2.0 ml), and water (2 × 2.0 ml). The ethereal solution was dried over Na_2SO_4 and concentrated in a vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–diethyl ether (4 : 1) gave 3-hydroxyoctan-2,7-dione (**6b**: 0.1233 g, 52%).

*3-Hydroxyoctan-2,7-dione (**6b**)*

IR (NaCl) 3463 and 1708 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 4.18$ (m, 1H), 3.58 (brs, 1H), 2.51 (t, 2H), 2.23 (s, 3H) and 1.58–1.66 (m, 4H). ^{13}C NMR ($CDCl_3$) $\delta = 209.8$, 208.6, 76.6, 42.9, 32.6, 29.9, 25.2 and 18.9. HRMS Found: m/z 140.0871 $[M - H_2O]^+$. Calc. for $C_8H_{12}O_2$: M, 140.0837.

*4-Hydroxydecan-3,8-dione (**7b**)*

IR (NaCl) 3504 and 1710 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 4.18$ (m, 1H), 3.56 (brs, 1H), 2.39–2.68 (m, 6H), 1.57–1.90 (m, 4H), 1.13 (t, 3H) and 1.05 (t, 3H). ^{13}C NMR ($CDCl_3$) $\delta = 209.8$, 208.6, 76.6, 41.5, 35.9, 32.9, 31.1, 18.9, 7.18 and 7.57. HRMS Found: m/z 186.1247 $[M]^+$. Calc. for $C_{10}H_{18}O_3$: M, 186.1256.

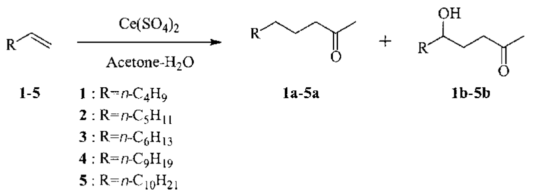
*3,6-Dimethyl-3-hydroxyoctan-2,7-dione (**8b**)*

IR (NaCl) 3469 and 1709 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta =$ 1.62–1.68 (m, 3H), 1.44 (s, 3H), 1.43 (m, 3H), 1.34 (t, 2H), 1.25 (s, 3H), 0.85 (d, 3H). ^{13}C NMR ($CDCl_3$) $\delta = 212.2$, 212.1, 84.0, 36.7, 31.8, 26.8, 23.7 20.7, 18.4 and 16.6. HRMS Found: m/z 168.1144 $[M - H_2O]^+$. Calc. for $C_{10}H_{16}O_2$: M, 168.1150.

RESULTS AND DISCUSSION

The reaction of alkenes **1**–**5** with CS in acetone–H_2O under reflux for 5 h gave 2-oxo- (**1a**–**5a**)[13–15] and 2-oxo-5-hydroxy derivatives (**1b**–**5b**)[16,17] (Scheme 1). These results are summarized in Table 1.

The IR spectrum of **3a** showed absorption at 1718 cm^{-1} (C=O). The ^1H NMR spectra exhibited a singlet at δ 2.13 (3H, $COCH_3$). The ^{13}C NMR spectra exhibited a signal at 209.3 ppm due to the C=O group. The CI mass spectrum of **3a** showed an $[M + H]^+$ peak at m/z 171. Therefore, compound **3a** was identified to be 2-undecanone. Compound **3b** showed



Scheme 1.

Table 1. The relationship between $Ce(SO_4)_2$ and selectivity

Run[a]	Substrate	CS (mol equiv.)	Product (ratio)[b]	Yield (%)
1	**1**	2.0	**1a/1b** (87/13)	72
2	**2**	2.0	**2a/2b** (89/11)	83
3	**3**	0.2	**3a/3b** (99/1)	39
4	**3**	0.5	**3a/3b** (94/6)	42
5	**3**	1.0	**3a/3b** (93/7)	73
6	**3**	1.5	**3a/3b** (90/10)	80
7	**3**	2.0	**3a/3b** (86/14)	98
8	**4**	2.0	**4a/4b** (92/8)	96
9	**5**	2.0	**5a/5b** (89/11)	97

[a] Substrate (2.0 mmol), CS (0.4–4.0 mmol), acetone (10.5 ml) and H_2O (1.5 ml) were employed under reflux for 5 h.

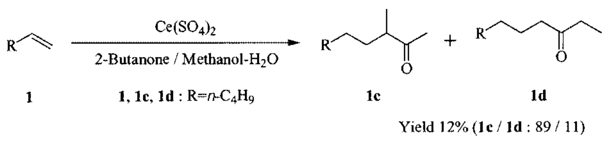
[b] The product ratios were determined by ^1H NMR. All products were identified by satisfactory spectral data (IR, ^1H NMR, ^{13}C NMR and mass spectrometry).

absorptions at 3423 (OH) and 1716 cm^{-1} (C=O) in its IR spectrum. The ^1H NMR spectra exhibited the presence of methyl groups at δ 2.17 (3H, $COCH_3$) and hydroxyl groups at δ 4.18 (1H, m, CH) and 3.57 (1H, brs, OH). The ^{13}C NMR spectra exhibited signals at 209.9 (C=O) and 71.3 ppm (C–OH). Therefore, compound **3b** was identified to be 5-hydroxy-2-undecanone.

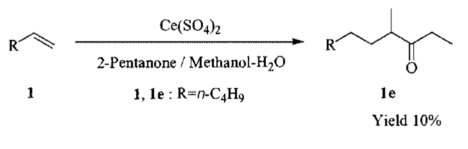
On the basis of these results, it was found that the reaction gives the 2-oxo- **1a**–**5a** and the 2-oxo-5-hydroxy derivatives **1b**–**5b** from olefins **1**–**5** and acetone–H_2O using CS. Under the reaction conditions using CS (0.4 mmol:0.2 mol equiv.), 2-oxo derivatives were obtained selectively. In the case of CS (4.0 mmol:2.0 mol equiv.), the yield of product rose to 98%, and the selectivity of the 2-oxo-5-hydroxy derivative was increased.

In addition to this reaction using acetone, it was found that the reaction of olefins with CS using 2-butanone or 3-pentanone in methanol–H_2O afforded 2-oxo-3-methyl- (**1c**)[18] and 3-oxo- (**1d**)[19] or 3-oxo-4-methyl derivatives (**1e**), respectively (Schemes 2 and 3). From these results, it was found that this reaction gave adducts from olefins and carbonyl compounds. However, the yields of products were poor. It is considered that the yields of products seem to depend on the solubility of CS in carbonyl compounds.

We further examined the reaction conditions to improve the yields of 2-oxo-5-hydroxy derivatives. From these results in Table 1, under these reaction conditions using CS (4.0 mmol:2.0 mol equiv.), the ratios of acetone–H_2O are changed (Table 2). As can be seen from Table 2, it was found that the formation of 2-oxo-5-hydroxy derivatives requires H_2O. In addition, the reaction of 1-octene (**3**) with CS in acetone without H_2O did not occur. Also, the reaction using 2-oxo derivatives as substrate did not afford 2-oxo-5-hydroxy derivatives. From these results, it seems that cerium(IV) and H_2O probably play an important role in this reaction mechanism, and the formation of 2-oxo-5-hydroxy derivatives simultaneously proceeds in this addition reaction of 2-oxo derivatives.



Scheme 2.



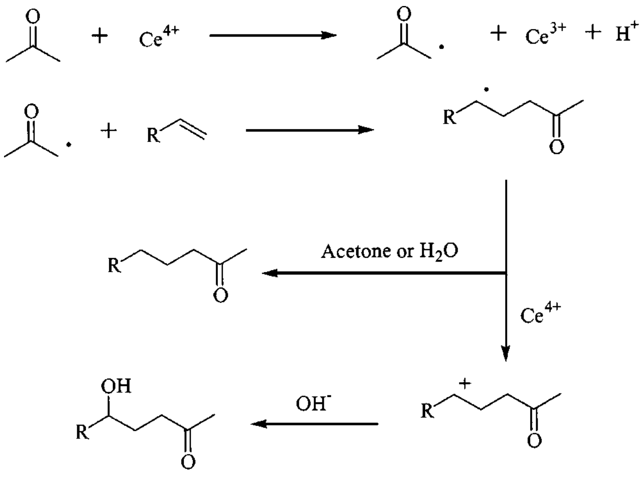
Scheme 3.

Table 2. Reaction of 1-octene (3) with CS in acetone–H_2O

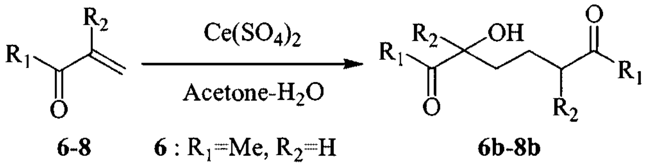
Run[a]	Substrate	Acetone: H_2O	Product (ratio)[b]	Yield (%)
1	**3**	1:3	**3a**/**3b** (72/28)	31
2	**3**	1:1	**3a**/**3b** (75/25)	68
3	**3**	3:1	**3a**/**3b** (80/20)	86
4	**3**	5:1	**3a**/**3b** (83/17)	97
5	**3**	7:1	**3a**/**3b** (86/14)	98
6	**3**	10:1	**3a**/**3b** (87/13)	92

[a] Reaction conditions: 1-octene (3) (2.0 mmol), CS (4.0 mmol), acetone (3.0–11.4 ml) and H_2O (0.6–12.0 ml) were employed under reflux for 5 h.

[b] The product ratios were determined by ^1H NMR. All products were identified by satisfactory spectral data (IR, ^1H NMR, ^{13}C NMR and mass spectrometry).



Scheme 4. Proposed reaction mechanism.



6-8 **6** : R_1=Me, R_2=H **6b-8b**
7 : R_1=Et, R_2=H
8 : R_1=Me, R_2=Me

Scheme 5.

Hieba and Dessaus reported that the reaction of olefins and acetone using cerium(IV) or manganese(III) acetates gave the corresponding 2-oxo, 2-oxo-5-acetoxy- and β,γ-unsaturated ketone. On the basis of this reaction mechanism, and from these results, we propose the reaction mechanism shown in Scheme 4. First, a radical species is generated by cerium(IV) from the carbonyl compounds. In the presence of olefins, radical adducts are formed; subsequently, a part of the radical adducts affords 2-oxo derivatives. Also, a part of the radical

Table 3. Reaction of α,β-unsaturated ketones with CS in acetone–H_2O

Run[a]	Substrate	Time (h)	Product (%)[b]
1	**6**	1	**6b** (52)
2	**7**	3	**7b** (34)
3	**8**	6	**8b** (19)

[a] Reaction conditions: α,β-unsaturated ketones (3.0 mmol), CS (0.3 mmol), acetone (10.0 ml) and H_2O (1.0 ml) were employed under reflux.

[b] Determined by gas chromatography. All products were identified by satisfactory spectral data (IR, ^1H NMR, ^{13}C NMR and mass spectrometry).

adducts oxidized by excess cerium(IV) gave 2-oxo-5-hydroxy derivatives.

Moreover, it is interesting that the reaction of α,β-unsaturated ketones **6**–**8** with CS in acetone–H_2O under reflux yielded the corresponding 2,6-dioxo-5-hydroxy or 3,8-dioxo-7-hydroxy derivatives **6b**–**8b** (Scheme 5, Table 3).

In conclusion, this reaction demonstrates the use of CS, and provides a new and simple synthetic method for 2-oxo-5-hydroxy derivatives using H_2O.

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