

Esterification of alkene with cerium(IV) sulfate in carboxylic acid[†]

C. Akira Horiuchi^{a*}, Tomoaki Fukushima^a, Noriyuki Furuta^a,
Wen Chai^a, Shun-Jun Ji^b, Yoshikazu Saito^a, Chikao Hashimoto^c,
T. Tomoyoshi Takahashi^c, Takashi Sugiyama^d, Akinori Muto^e,
Yusaku Sakata^e and Sukekatsu Nozaki^f

^aDepartment of Chemistry, Rikkyo (St. Paul's) University, Nishi-Ikebukuro, Toshima-Ku, Tokyo 171-8501, Japan

^bDepartment of Chemistry, Suzhou University, 1 Shizi St. Suzhou, Jiangsu 215006, P. R. China

^cDepartment of Chemistry, Jikei University, School of Medicine, Kokuryo-cho, Chofu-shi, Tokyo 182-8570, Japan

^dInstitute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

^eDepartment of Applied Chemistry, Okayama University, Faculty of Engineering, Tsushima Naka, Okayama City, Okayama 700-8530, Japan

^fFaculty of Pharmaceutical Science, Josai University, Sakado, Saitama 350-0295, Japan

Reaction of alkenes [cyclohexene (1), cycloheptene (2), cyclooctene (3), 1-heptene (4), 1-octene (5), styrene (6), 1,7-octadiene (7), indene (8), and 1,2-dihydronaphthalene (9)] with cerium(IV) sulfate (CS) in carboxylic acids [formic acid, acetic acid, and propionic acid] readily yielded the corresponding carboxylic esters. This addition reaction follows the Markovnikov rule. This reaction provides a new simple method for preparing carboxylic esters from alkenes. It was also found that this method is useful for formylation.

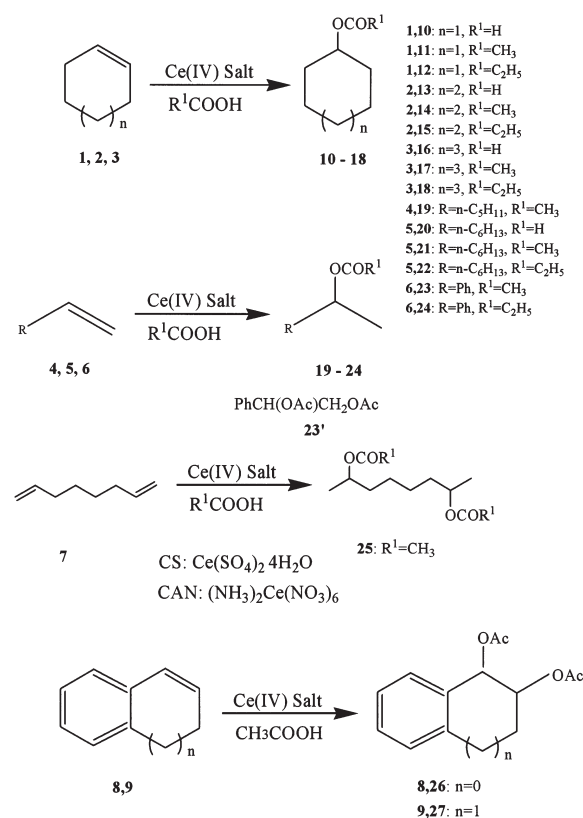
Keywords: esterification, alkene, cerium(IV) sulfate, formylation

The esters of carboxylic acids are an important group of compounds since they are used for a wide variety of chemical reactions and are also natural products.

Esters may be formed directly from carboxylic acids or in other cases the alkoxycarbonyl group, -COOR, is derived from a less directly related functional group. Esters are formed by the reaction between a carboxylic acid and an alcohol. However, no formylation of alcohol with the anhydride and the acid chloride of formic acid has been reported in the literature up to the present time due to the instability of these reagents.¹

Recently Barluenga *et al.* reported that the reaction of different Vilsmeier-Haack adducts with alcohols gives the corresponding formic acid esters.² It is known that preparations of carboxylic esters by the addition of carboxylic acids to alkenes are usually catalysed by protons or Lewis acids. Moreover, it is known that the reaction of alkenes with metallic acylates in carboxylic acids yields the corresponding allylic esters.¹ More recently, it has been reported that the exchange reaction of alcohols with esters gave desired esters, although this method was found not to be applicable to cyclic formate esters.³

In connection with our studies, we had found: the synthesis of steroidal *trans*-iodoacetates using iodine-copper(II) acetate;⁴ a new synthesis of *cis*-diols from olefins using iodine-copper(II) acetate;⁵ and a new alkoxyiodination and nitroiodination of olefins using iodine-ammonium cerium(IV) nitrate.⁶ Still earlier, we reported that the reaction of cycloalkenes with iodine-cerium(IV) sulfate (CS) in acetonitrile-water (10:1) at 50°C, yielded *trans*-iodohydrins preferentially⁷ and the reaction of styrene derivatives with CS in methanol yielded 1,2-dimethoxy compounds.⁸



We now report that the reaction of alkenes [cyclohexene (1), cycloheptene (2), cyclooctene (3), 1-heptene (4), 1-octene (5), styrene (6), 1,7-octadiene (7), indene (8), and 1,2-dihydronaphthalene (9)] with CS in carboxylic acids gave the corresponding carboxylic esters in good yields. These results are summarised in Table 1.

* To receive any correspondence.

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Addition of carboxylic acid to alkenes using cerium(IV) salt

| Run | Substrate | Solvent | Temp/h | Ce(IV) Salt (Mol.equiv.) | Product(%) ^a |
|-----|-----------|---------|-----------|--------------------------|--|
| 1 | 1 | HCOOH | 80°C/10 | CS(0.5) | 10(58) ^{2,14,15} |
| 2 | 1 | AcOH | 80°C/10 | CS(1) | 11(51) ^{9,10} |
| 3 | 1 | AcOH | 80°C/8 | CAN(1) | 11(25) ^{9,10} |
| 4 | 1 | EtCOOH | 80°C/10 | CS(0.5) | 12(15) ¹⁸ |
| 5 | 2 | HCOOH | 50°C/14 | CS(0.5) | 13(63) ⁹ |
| 6 | 2 | AcOH | 80°C/5 | CS(1) | 14(56) ⁹ |
| 7 | 2 | EtCOOH | 80°C/10 | CS(0.5) | 15(27) ²⁵ |
| 8 | 3 | HCOOH | 50°C/5 | CS(0.25) | 16(79) ¹⁹ |
| 9 | 3 | AcOH | 80°C/8 | CS(0.5) | 17(60) ^{b,9,11} |
| 10 | 3 | AcOH | 80°C/8 | CS(1) | 17(43) ^{9,11} |
| 11 | 3 | EtCOOH | 80°C/10 | CS(0.5) | 18(18) ¹¹ |
| 12 | 4 | AcOH | reflux/10 | CS(0.5) | 19(8) ²⁵ |
| 13 | 4 | AcOH | reflux/10 | CS(1) | 19(15) ²⁵ |
| 14 | 5 | HCOOH | 80°C/10 | CS(0.5) | 20(62) ^{2,3,12,14,15} |
| 15 | 5 | AcOH | reflux/15 | CS(0.5) | 21(30) ^{13,15} |
| 16 | 5 | EtCOOH | reflux/10 | CS(0.5) | 22(18) ²⁵ |
| 17 | 6 | AcOH | 50°C/13 | CS(0.5) | 23(78) ¹⁶ |
| 18 | 6 | AcOH | 50°C/8 | CS(1) | 23(27) ^{b,16} 23'(57) ^{b,17,20,22} |
| 19 | 6 | AcOH | 50°C/4 | CS(2) | 23(6) ^{b,16} 23'(68) ^{b,17,20,22} |
| 20 | 6 | AcOH | reflux/16 | CAN(0.5) | 23(1) ^{b,16} 23'(10) ^{b,17,20,22} |
| 21 | 6 | AcOH | reflux/16 | CAN(1) | 23'(73) ^{b,17,20,22} |
| 22 | 6 | AcOH | reflux/16 | CAN(2) | 23'(47) ^{b,17,20,22} |
| 23 | 6 | EtCOOH | 80°C/10 | CS(0.5) | 24(60) ²¹ |
| 24 | 7 | AcOH | reflux/5 | CS(0.5) | 25(59) ²⁰ |

Reaction conditions: substrate(2.0mmol) and solvent (10ml).

^aIsolated yield. ^bDetermined by GLC analysis using *n*-dodecane as an internal hydrocarbon standard.

Table 2 Addition of acetic acid to indene or 1,2-dihydronaphthalene using cerium(IV) salt

| Run | Substrate | Solvent | Temp/h | Ce(IV) Salt (Mol.equiv.) | Product(%) ^a | (<i>cis/trans</i>) ^b |
|-----|-----------|---------|--------------|--------------------------|-------------------------|-----------------------------------|
| 1 | 8 | AcOH | 50°C / 4 | CS(0.5) | 26(18) ²³ | (71/29) |
| 2 | 8 | AcOH | 50°C / 4 | CS(1) | 26(53) ²³ | (76/24) |
| 3 | 8 | AcOH | 50°C / 4 | CS(2) | 26(71) ²³ | (78/22) |
| 4 | 8 | AcOH | R.T. / 24 | CS(0.5) | 26(16) ²³ | (75/25) |
| 5 | 8 | AcOH | R.T. / 24 | CS(1) | 26(48) ²³ | (72/28) |
| 6 | 8 | AcOH | R.T. / 24 | CS(2) | 26(74) ²³ | (73/27) |
| 7 | 8 | AcOH | reflux / 2.5 | CAN(1) | 26(23) ²³ | (72/28) |
| 8 | 8 | AcOH | reflux / 2.5 | CAN(2) | 26(51) ²³ | (73/27) |
| 9 | 9 | AcOH | 50°C / 4 | CS(0.5) | 27(17) ²⁴ | (33/67) |
| 10 | 9 | AcOH | 50°C / 4 | CS(1) | 27(48) ²⁴ | (40/60) |
| 11 | 9 | AcOH | 50°C / 4 | CS(2) | 27(67) ²⁴ | (45/55) |
| 12 | 9 | AcOH | R.T. / 24 | CS(1) | 27(20) ²⁴ | (37/63) |
| 13 | 9 | AcOH | R.T. / 24 | CS(2) | 27(38) ²⁴ | (41/59) |
| 14 | 9 | AcOH | R.T. / 24 | CAN(1) | 27(23) ²⁴ | (50/50) |
| 15 | 9 | AcOH | Reflux / 2.5 | CAN(2) | 27(51) ²⁴ | (50/50) |

Reaction conditions: Substrate (2.0mmol) and solvent (10ml).

^aDetermined by GLC analysis using *n*-dodecane as an internal hydrocarbon standard.

^bRatios of *cis* and *trans* were determined by ¹H NMR spectrum.

As can be seen in Table 1, the reaction proved to have general applicability in the synthesis of the cyclic formate. The synthesis described in this paper is the most convenient procedure for preparing cyclic formate esters.

In the case of styrene (**6**) or 1,7-octadiene (**7**) with CS in formic and acetic acid at room temperature or 80°C, the corresponding diesters were obtained. So, we tried the reaction of indene (**8**) and 1,2-dihydronaphthalene (**9**) with CS in acetic acid. These results are summarised in Table 2.

As can be seen in the Table 2, it was found that this reaction provides a new simple method for the preparing carboxylic diesters, especially the *cis*-diacetate from **8**.

This is the first time that direct formylation of alkene has been successfully accomplished. It is particularly noteworthy that this reaction affords a new synthetic method for formylation of alkenes.

Experimental: A mixture of cyclooctene (**3**)(220 mg, 2.0 mmol) and cerium(IV) sulfate (202 mg, 0.5 mmol) in formic acid (10 ml) was stirred at 50 °C for 5 h. The precipitated cerium salt was removed by filtration. The reaction mixture was poured into water and extracted with diethyl ether (50 ml × 3). The ethereal solution was washed with aqueous sodium hydrogen carbonate (10 ml × 5) and water (10 ml × 3), dried and then evaporated. The resulting oil gave pure product **16** (247 mg, 63%). All compounds are determined by IR, ¹H NMR, ¹³C NMR, and GC-MS spectra.

The authors wish to express Ms. Kazue Satoh, for their measurement of the mass spectra. This work was supported by Rikkyo University Grant for the Promotion of Research.

Received 15 October 2002; accepted 6 December 2002
Paper 02/1606

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- 25 Spectroscopic and analytical data. Compound **15**: Colourless oil; $\nu_{\max}/\text{cm}^{-1}$ (NaCl) 1734 and 1190; δ_{H} (CDCl_3) 1.12(t, 3H), 1.60–1.71(m, 10H), 2.29(q, 2H), and 4.92–4.95(m, 1H); δ_{C} (CDCl_3) 9.2, 22.9, 28.3, 30.4, 33.9, 74.9, and 173.9. HRMS (EI): calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: 170.1307; found: 170.1325. Compound **19**: Colourless oil; $\nu_{\max}/\text{cm}^{-1}$ (NaCl) 1726 and 1186; δ_{H} (CDCl_3) 0.83–1.36(m, 16H), 5.01–5.05(m, 1H), and 8.04(s, 1H); δ_{C} (CDCl_3) 14.1, 20.0, 22.6, 25.4, 29.1, 31.8, 36.0, 71.0, and 160.9. HRMS (EI): calcd for $\text{C}_9\text{H}_{18}\text{O}_2$: 158.1307.; found: 158.1352. Compound **22**: Colourless oil; $\nu_{\max}/\text{cm}^{-1}$ (NaCl) 1734 and 1190; δ_{H} (CDCl_3) 0.88(t, 3H), 1.13(t, 3H), 1.20(d, 2H), 1.25–1.40(m, 10H), 2.30(q, 2H), and 4.87–4.94(m, 1H); δ_{C} (CDCl_3) 9.3, 14.0, 20.0, 22.6, 25.4, 28.0, 29.1, 31.8, 36.0, 70.8, and 174.2. HRMS (EI): calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2$: 186.1620; found: 186.1608.