SHORT PAPER

J. Chem. Research (S),
2000, 172–173

Cerium (IV) sulfate mediated oxidative addition of 1-phenylcycloalkenes and styrene derivatives in methanol: synthesis of 1,2-dimethoxy compounds

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The reaction of 1-phenylcycloalkenes and derivatives of styrene with cerium(IV) sulfate tetrahydrate in methanol leads to the formation of 1,2-dimethoxy compounds (54–89%).

The importance of cerium(IV) salts as an oxidizing agent for organic compounds has been studied considerably over the past several years.[1] Cerium(IV) compounds are considered to be the most notable oxidants in the lanthanide group. There are several reports of their synthetic applications on organic functional oxidation.[2]

1-Aryl-1,2-dimethoxyalkane is usually prepared by one of the following methods: oxidation of styrene derivatives with oxidizing agents catalysed by diaryl di-tellurides,[3] electrochemical cleavage of double bonds in 1-phenylcycloalkenes and 1,2-benzo-1,3-cycloalkadienes,[4] photochemical electron-transfer reaction between styrene derivatives and metal ions in methanol,[5] and catalytic etherification of phenethyl alcohol with dimethyl sulfate.[6] 1,2-Dimethoxyalkane also has been obtained as a by-product by reacting 1-phenylcycloalkenes with ammonium cerium (IV) nitrate (CAN) in methanol.[7] We have investigated the reaction of 2-alkylcycloalkanone with I_2–Ce(IV) salts in alcohols (methanol, ethanol, 1-propanol, and 2-propanol) yields the corresponding oxo ester.[8] We have also reported the oxidative cleavage reaction of cycloalkanones with cerium(IV) sulfate tetrahydrate (CS) in alcohols and acetic acid, which gave the corresponding alkyl ester or diester of carboxylic acid.[9] Through our studies, we have found that I_2–CS and CS are useful reagents for the synthesis of a large number of ester compounds.

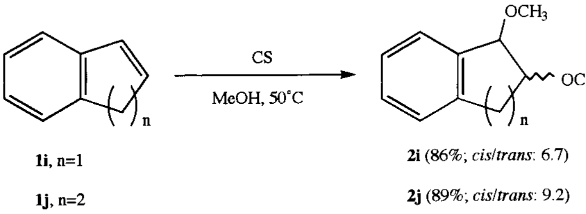
In this paper, we would like to report that the reaction of 1-phenylcycloalkenes (**1a, 1b** and **1c**), 1-methylcyclohexene (**1d**), styrene derivatives (**1e, 1f, 1g** and **1h**), indene (**1i**) and 1,2-dihydronaphthalene (**1j**) with CS in methanol leads to the formation of 1,2-dimethoxy compounds (54–89%) by using the properties of CS having lower solubility in organic solvent and weaker oxidative property compared with CAN.

Results and discussion

The reaction of 1-phenylcycloalkenes with CS in methanol gave the corresponding 1,2-dimethoxy compounds in good yields. The results are summarized in Table 1. It was found that the 1-phenylcycloalkenes (**1a**–**1c**) can react with CS in methanol. Thus, oxidative 1,2-addition of methoxy group to carbon–carbon double bond activated by phenyl group took place. Moreover, it was found that *cis*-isomer was formed preferentially, which was determined by comparison of the ^{1}H and ^{13}C NMR spectra with the result reported.[4] In the case of 1-methylcyclohexene (**1d**), no 1,2-addition reaction occurred, but oxidation product, 2-methoxy-2-methylcyclohexanone (**2d**) was obtained. The results show that the phenyl at cycloalkene is necessary for the addition of methoxy to carbon–carbon double bond. In ethanol, the oxidative reaction of 1-phenylcyclohexene (**1b**) gave 2-ethoxy-2-phenylcyclohexanone (**3b**).

The styrene and ring-methyl substituted styrene also reacted with CS in methanol. The results are summarized in Table 2. It was found that the vinyl group of the styrene reacts with CS in methanol and the derivative of (1,2-dimethoxyethyl)benzene was obtained in good yield. The substrates **1f, 1h** having methyl group at *ortho*- or *para*-position have higher reactivity than styrene. In the case of *m*-methylstyrene (**1g**), *m*-methylbenzaldehyde was also obtained.

Indene (**1i**) and 1,2-dihydronoaphthalene (**1j**) were also treated with CS in methanol and the corresponding *cis*-1,2-dimethoxy compounds were obtained in good yields (Scheme 1).



Scheme 1

By comparison with the reaction of CAN,[7] it was found that by reacting CS with the same substrate and in the same solvent (MeOH), oxidative fragmentation did not occur, but the oxidative addition was found and the 1,2-dimethoxy compounds was obtained. Therefore, there is a difference between CS and CAN in reactivity under the same reaction conditions.

Tables 1 and 2 also indicated that 1,2-dimethoxy compounds were obtained by reacting 1-phenylcycloalkenes and styrene with ammonium cerium(IV) sulfate (CAS) in methanol, but yields and stereoselectivity were lower than CS.

In conclusion, we have encountered a novel Ce(IV) mediated oxidative addition of 1-phenylcycloalkenes and styrene resulting in an efficient and direct synthesis of 1,2-dimethoxy compounds. It is noteworthy that the method reported here has high stereoselectivity and CS has different property with CAN under the reaction conditions mentioned above.

Experimental

IR spectra were measured using a Jasco FT./IR 230. NMR spectra were measured on a JEOL GSX 400 spectrometer with the samples dissolved in deuteriochloroform with TMS as the internal standard.

Typical procedure: Reaction of 1-phenylcyclohexene with CS in MeOH: A mixture of 1-phenylcyclohexene (**1b**) (0.316 g, 2.0 mmol) and cerium(IV) sulfate tetrahydrate (1.62 g, 4.0 mmol) in methanol (20 ml) was stirred at 50 °C for 5 h. The white precipitate was removed by filtration and the reaction solvent was removed under reduced pressure. The residue was poured into water (20 ml) and extracted with diethyl ether (2 × 25 ml). The ethereal solution was

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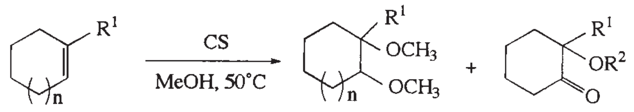
[*] To receive any correspondence.

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



1a: n=0, R^1=Ph
1b: n=1, R^1=Ph
1c: n=2, R^1=Ph
1d: n=1, R^1=Me

2a n=O, R^1=Ph
2b:n=1, R^1=Ph
2c: n=2, R^1=Ph

3b: R^1=Ph, R^2=Et
2d:R^1=R^2=Me

Table 1 CS mediated oxidative addition of 1-phenylcycloalkenes in MeOH[a]

Run	Sub-strate	Cerium (IV) Salt	Temp (°C)	Time (h)	Products and yields (%)[b] (*cis/trans*)
1	**1a**	CS	50	5	**2a** 75 (8.8)
2	**1a**	CAS	50	10	**2a** 18 (5.5)
3	**1b**	CS	rt	20	**2b** 25 (7.2)
4	**1b**	CS	50	5	**2b** 86 (13.3)
5	**1b**	CAS	rt	20	**2b** 5 (4.2)
6	**1b**	CAS	50	10	**2b** 36 (6.5)
7[c]	**1b**	CS	65	15	**3b** 32
8	**1c**	CS	50	6	**2c** 71 (9.6)
9	**1c**	CAS	50	10	**2c** 23 (5.6)
10	**1d**	CS	50	5	**2d** 23 (5.6)
11	**1d**	CAS	50	10	**2d** 0

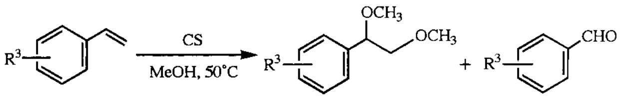
[a] Reaction conditions: substrate (2.0 mmol), CS (4.0 mmol), and MeOH (20 ml) were employed.
[b] Isolated yield. [c] The solvent was EtOH.

washed successively with aq. solution of NaCl (10 ml), aq. sodium hydrogencarbonate solution (10ml) and water (10ml). The organic layer was dried over Na_2SO_4 and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane-ether (4:1) gave *cis*-1,2-dimethoxyl-1-phenylcyclohexane (*cis*-**2b**) as colourless oil (0.351 g, 80%) and *trans*-1,2-dimethoxyl-1-phenylcyclohexane (*trans*-**2b**) as colourless oil (0.032g, 6%).

Spectroscopic and analytical data. **2f**: Colourless oil; υ_{max}/cm^{-1} (NaCl) 2926 and 1101; δ_H (CDC1$_3$) 7.16-7.40 (m, 4H), 4.68 (dd, *J*=2.9, 5.8Hz, 1H), 3.54 (t, *J*=8.8Hz, 1H), 3.37 (dd, *J*=2.9, 8.0Hz, 1H), 3.41 (s, 3H), 3.28 (s, 3H), and 2.36 (s, 3H); δ_C (CDCl$_3$) 136.6, 135.7, 130.5, 127.6, 126.3, 126.2, 79.6, 76.5, 59.2, 56.9, and 19.1; MS (EI): *m/z* 180 (M+), 149, 135, 119 and 91; MS (CI): *m/z* 181 ([M+1]+)

2g: Colourless oil; υ_{max}/cm^{-1} (NaCl) 2925 and 1106; δ_H (CDC1$_3$) 7.11–7.27 (m, 4H), 4.36 (dd, *J*=3.2, 4.8Hz, 1H), 3.59 (t, *J*=8.4Hz, 2H), 3.43 (d, *J*=3.3Hz, 1H), 3.40 (s, 3H), 3.29 (s, 3H), and 2.36 (s, 3H); δ_C (CDC1$_3$) 138.7, 138.1, 128.8, 128.4, 127.6, 124.1, 83.0, 77.3, 59.2, 57.0, and 21.4; MS (EI): *m/z* 180 (M+), 149, 135, 119 and 91; MS (CI): *m/z* 181 ([M+1]+).

This work was supported by Rikkyo University Grant for the Promotion of Research.



1e: R^3=H
1f: R^3=*o*-Me
1g: R^3=*m*-Me
1h: R^3=*p*-Me

2e: R^3=H
2f: R^3=*o*-Me
2g: R^3=*m*-Me
2h: R^3=*p*-Me

3e: R^3=H
3f: R^3=*o*-Me
3g: R^3=*m*-Me
3h: R^3=*p*-Me

Table 2 CS mediated oxidative addition of styrenes in MeOH[a]

Run	Sub-strate	Cerium (IV) Salt	Temp (°C)	Time (h)	Product (%)[b]
1	**1e**	CS	50	5	**2e** (54) + **3e** (t)[c]
2		CAS	50	10	**2e** (8)
3	**1f**	CS	50	5	**2f** (68) + **3f** (t)
4		CAS	50	10	**2f** (22)
5	**1g**	CS	50	8	**2g** (61) + **3g** (5)
6		CAS	50	15	**2g** (16)
7	**1h**	CS	rt	20	**2h** (23)
8		CS	50	5	**2h** (71) + **3h** (t)
9		CAS	rt	20	**2h** (6)
10		CAS	50	10	**2h** (28)

[a] Reaction conditions: substrate (2.0 mmol), CS (4.0 mmol), and MeOH (20 ml) were employed.
[b] Isolated yield. [c] t=trace

Received 12 February 2000; accepted 7 April 2000
Paper 99/132

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