PHOTOOXYGENATION (*ELECTRON TRANSFER*) OF SILYL ENOL ETHERS DERIVED FROM 1-INDANONE: SILYL GROUP AND MEDIUM EFFECTS ON THE COMPETITIVE FORMATION OF 3-SILOXY-1,2-DIOXETANE AND α–PEROXY KETONE

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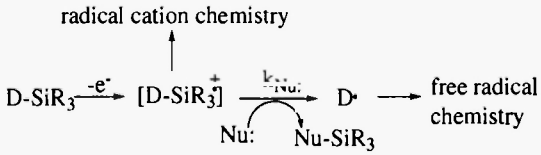
Abstract

Photooxygenation (electron transfer) sensitized by 9,10-dicyanoanthracene(DCA)/bipyridyl(BP) of silyl enol ethers **1** (SiR_3 = TMS, TES, TBDMS) was performed. The oxygenation reaction was found to be controlled by the proper choice of the silyl group and the reaction medium. Namely, (1) by selecting the silyl group (SiR_3 = TBDMS) and the non-nuclephilic medium (CH_2Cl_2), the preferred formation of 3-hydroxy lactone **2** was achieved, which is derived from 3-siloxy-1,2-dioxetane **5**; (2) by adding the proper nucleophile (in this case, MeOH) in the reaction medium, the selective formation of α-peroxy indanone **7** has been observed when the triethylsilyl (TES) group was selected for the reaction.

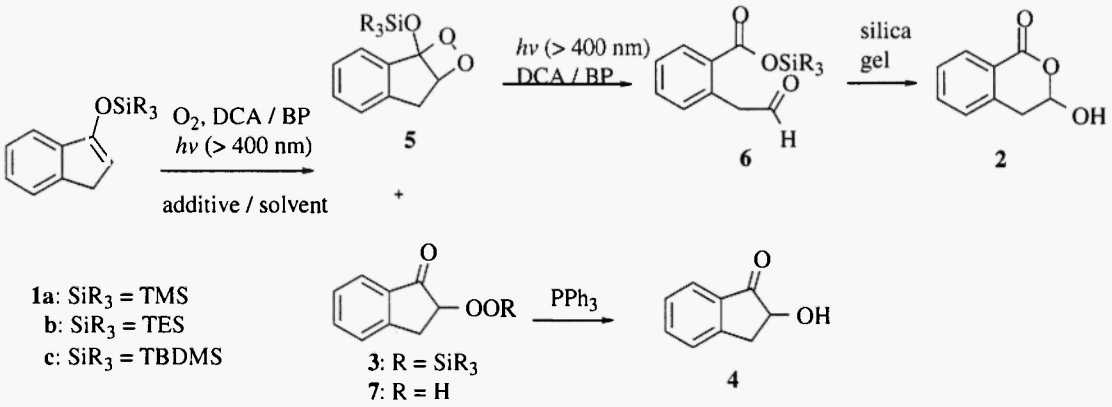
Introduction

Organosilanes ($D\text{-}SiR_3$) have been considered as one of the powerful donors in electron transfer chemistry due to their relatively low oxidation-potentials. A number of donor profile reactions has been investigated in terms of both the synthetic and mechanistic points of view.[1-5] Recently, the nucleophile-assisted desilylation (S_N2) mechanism of the cation radicals ($D\text{-}SiR_3^{\bullet+}$) was proved by Dinnocenzo et al., affording the free radical species (D•) [Scheme 1].[6] Namely, the rate constant (k_{Nu}) has been found to be largely dependent upon the steric circumstances of both the silyl group and the nucleophile.



Scheme 1

From the synthetic point of view, it would be very useful if the reaction (*cation radical chemistry* vs *free radical chemistry*) can be controlled by the proper choice of the silyl group and the reaction medium (solvent, additive). In this respect, we have decided to investigate the electron transfer photooxygenation[7] of silyl enol ethers **1** derived from 1-indanone, in which the silyl group can be easily changed [Scheme 2].



Scheme 2

Experimental

General aspects

^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EX-270 spectrometer at 270 MHz and 67.8 MHz, respectively. ^1H NMR chemical shifts are given in ppm (δ_H) using residual $CHCl_3$ (δ 7.26) in the perdeuterated solvent as the internal standard. [s (singlet), d (doublet), t (triplet) and m (complex patternt)]. ^{13}C NMR chemical shifts are given in ppm (δ_C) relative to the internal standard $CDCl_3$ (δ 77.00). IR spectra were recorded on a Hitachi 260-30 spectrophotometer. Mass spectrometric data were obtained by using a JEOL JNS-BX 303-HF mass spectrometer. Elemental analyses were carried out by Analytical Division of the Faculty of Engineering, Osaka University.

Cyclic Voltammetry

The cyclic voltammetry measurements were performed on a BAS CV-50W in deaerated acetonitrile containing 0.10 M Et_4NClO_4 as a supporting electrolyte at 293 K. With a scan rate of 400 mV / s, silyl enol ethers **1a-c** showed irreversible oxidation. The measured peak oxidation potentials of **1a-c**, **1a**: E_p = 0.98 V, **1b**: E_p = 0.96 V, **1c**: E_p = 0.95 V, were recorded with respect to Ag / Ag^+. The oxidation potentials E_p vs. SCE are found by adding 0.30 V.[8]

Photolyses

Photolyses (> 400 nm) were conducted with a Eikohsha 500 W high-pressure mercury lamp though a $CuSO_4$ solution in aq. NH_3.

Preparation of silyl enol ethers **1**.

Silyl enol ethers **1** were prepared similarly by a reported method (isolated yields, 60-80%).[9] Spectroscopic data were described previously.[10]

Photooxygenation (*electron transfer*) of silyl enol ethers **1**

A solution of silyl enol ether **1** (2.4 mmol) in a solvent (50 cm^{-3}) was irradiated (> 400 nm) in the presence of DCA (0.12 mmol) and BP (2.4 mmol) at 0 °C for 3 h under oxygen atmosphere. After the solvent was removed under reduced pressure at 0 °C, the reaction mixture was treated with PPh_3 in benzene. The products, lactone **2** and α-hydroxy indanone **4**, were isolated by using silica gel chromatography. The product yields (%) are reported in Table 1. The structure of the lactone **2**[11] and of the α-hydroxy ketone **4**[12] was confirmed by the NMR data reported previously.[10] NMR spectroscopic data measured in our conditions for the lactone **2** and the α-hydroxy ketone **4** are as follows.

3,4-Dihydro-3-hydroxy-1*H*-2-benzopyran-1-one **2.** δ_H (270 MHz; $CDCl_3$) 3.14 (dd, *J* 3.1 and 16.4, 1 H, C4-H), 3.34 (dd, *J* 3.3 and 16.4, 1 H, C4-H), 4.24 (br s, 1 H, OH), 5.95 (dd, *J* 3.1 and 3.3, 1 H, C3-H), 7.26-7.62 (m, 3 H, Ar-H), 8.10-8.13 (m, 1 H, Ar-H); δ_C (67.8 MHz; $CDCl_3$) 33.37 (C4), 95.42 (C3), 124.06 (Ar), 127.08 (Ar), 127.96 (Ar), 129.51 (Ar), 133.78 (Ar), 135.96 (Ar), 164.92 (C=O).

2,3-Dihydro-2-hydroxy-1*H*-indan-1-one **4.** δ_H (270 MHz; $CDCl_3$) 2.97 (br s, 1H, OH), 3.00 (dd, *J* 4.9 and 16.7, 1 H, C3-H), 3.58 (dd, *J* 8.1 and 16.7, 1 H, C3-H), 4.53 (dd, *J* 4.9 and 8.1, 1 H, C2-H), 7.37-7.47 (m, 2 H, Ar-H), 7.60-7.66 (m, 1 H, Ar-H), 7.74-7.78 (m, 1 H, Ar-H); δ_C (67.8 MHz; $CDCl_3$) 35.08 (C3), 74.07 (C2), 124.30 (Ar), 126.67 (Ar), 127.85 (Ar), 133.94 (Ar), 135.78 (Ar), 150.91 (Ar), 206.83 (C=O).

Photooxygenation of silyl enol ethers **1b,c** in the presence of MeOH (15 equiv.).

Adter irradiation (see above), the solvent was removed under reduced pressure at 0 °C, the crude mixture was subjected to column chromatography on silica gel. For the reaction of the silyl enol ether **1b** (SiR_3 = TES), α-hydroperoxy indanone **7** was isolated in 57% yield in almost pure form (ca. 90% from NMR analysis). The structure of the α-hydroperoxy indanone **7** was confirmed by its chemical transformation into the α-hydroxy indanone **4** upon treatment with triphenylphosphine (PPh_3). The yields for the other oxygenated products are given in Table 1 (entries 6 and 7).

2,3-Dihydro-2-hydroperoxy-1*H*-indan-1-one **7.** δ_H (270 MHz; $CDCl_3$) 3.33 (dd, *J* 4.6 and 17.3, 1 H, C3-H), 3.58 (dd, *J* 7.8 and 17.3, 1 H, C3-H), 4.91 (dd, *J* 4.6 and 7.8, 1 H, C2-H), 7.37-7.78 (m, 4 H, Ar), 10.08 (br s, 1 H, OOH); δ_C (67.8 MHz; $CDCl_3$) 30.83 (C3), 85.03 (C2), 124.39 (Ar), 126.79 (Ar), 127.98 (Ar), 132.15 (Ar), 136.15 (Ar), 151.39 (Ar), 203.77 (C=O).

Results and Discussion

Silyl enol ethers **1** (SiR_3 = TMS, TES, TBDMS) derived from 1-indanones were prepared by a method described elsewhere.[9] The oxidation potentials (E_p = ca. 1.2 V vs SCE in CH_3CN, see Experimental section) measured by cyclic voltammetry (CV) reveal that the electron transfer with the excited state of dicyanoanthracene (DCA, E_{red} = -0.89 V, ^1E_S = 2.88 eV)[7a,b] is feasible ($\Delta G_{et} < 0$). To exclude the intervention of singlet oxygen ($^1O_2$) sensitized by DCA, all of the photooxygenations were performed in the presence of biphenyl (BP) as a cosensitizer under oxygen atmosphere [Scheme 2].[13]

Table 1 DCA-sensitized Photooxygenation (*electron transfer*) of silyl enol ethers 1 derived from 1-indanone[a]

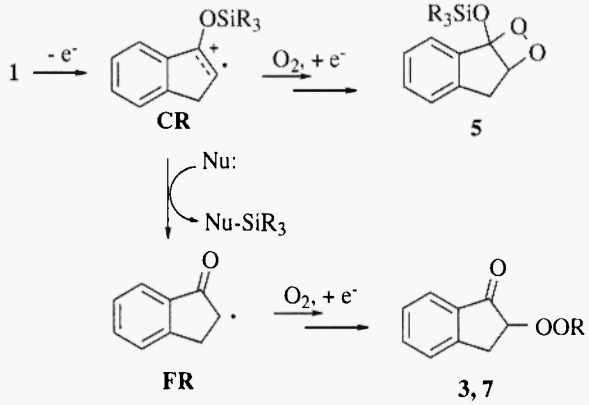
entry		silyl enol ether **1** SiR_3	solvent / additive	products and yields / %[b] **2**	**4**	ratios[c] **2 / 3**
1	**1a**	TMS	CH_2Cl_2	53	32	62 / 38
2	**1b**	TES	CH_2Cl_2	36	10	78 / 22
3	**1c**	TBDMS	CH_2Cl_2	50	10	83 / 17
4	**1a**	TMS	DMF	13	20	40 / 60
5	**1a**	TMS	CH_3CN	21	35	37 / 63
6	**1b**	TES	CH_2Cl_2 / MeOH[d]	7	57	11 / 89
7	**1c**	TBDMS	CH_2Cl_2 / MeOH[d]	67	13	84 / 16

[a] Photoreactions were run in the presence of DCA and BP under oxygen atmosphere at 0 °C. [b] Isolated yields after column chromatography on silica gel. [c] The ratios **2 / 3** were estimated from the product ratios of **2 / 4**. [d] The photooxygenation was performed in the presence of 15 equiv. of MeOH in CH_2Cl_2 at 0 °C. ca. 10 % of 1-indanone was recovered.

First of all, to examine the silyl group effects on the product distributions, the electron transfer photooxygenations ($h\nu$ > 400 nm) of silyl enol ethers **1** (SiR_3 = TMS, TES, TBDMS) were run in non-nucleophilic solvent, CH_2Cl_2 at 0 °C [entries 1-3 in Table 1]. The oxygenations were successfully occurred (3 h) to give the 3-hydroxy lactone **2** together with the α-peroxy indanone **3** [Scheme 2 and Table 1]. The structure of the α-peroxy indanone **3** was confirmed by its transformation into the α-hydroxy indanone **4** upon treatment with triphenylphosphine (PPh_3). To understand the mechanism for the formation of the lactone **2**, the dioxetane **5c** (SiR_3 = TBDMS) was prepared by using $^1O_2$[10] and irradiated under the electron-transfer oxygenation conditions ($h\nu$ > 400 nm, in the presence of DCA and BP). In fact, the dioxetane **5c** was unstable under these conditions and afforded quantitatively the keto ester **6c**, which was converted to the lactone **2** under the isolation conditions (silica gel). The product ratios of the lactone **2** and peroxy indanone **3** (**2 / 3**) were slightly dependent on the silyl group (SiR_3) [entries 1-3 in Table 1]. When the sterically hindered SiR_3 = TBDMS was used for the reaction, the increase of the dioxetane product, lactone **2**, was observed.

Next, the medium (solvent) effects on the product ratios **2 / 3** were investigated for the photooxygenation of silyl enol ether **1a** (SiR_3 = TMS) [entries 1,4,5 in Table 1]. Increasing the nucleophilicity of the solvent (from CH_2Cl_2 to DMF, CH_3CN) caused an increase of the yield of the α-peroxy indanone **3**.

Based on the silyl group and solvent effects on the product ratios of **2 / 3**, the mechanism for the formation of dioxetane **5** and α-peroxy indanone **3** may be hypothesized as shown in Scheme 3.



Scheme 3

The dioxetane **5** is mainly derived from the oxygenation of the cation radical (**CR**) generated by the electron transfer oxidation with DCA/BP (*cation radical chemistry*).[14,15] Alternatively, the α-peroxy indanone **3** can be formed from the reaction of the free radical (**FR**) with molecular oxygen (*free radical chemistry*). If the

mechanism is correct, the nucleophilic MeOH effects on the product ratios would be expected to increase the pathway of the free radical chemistry [entries 6,7 in Table 1].

The photooxygenations were performed in the presence of MeOH (15 equiv. to the silyl enol ether **1**) in CH_2Cl_2 [entries 6,7 in Table 1]. In the case of the silyl enol ether **1a** (SiR_3 = TMS), the desilylation by MeOH was observed to give 1-indanone without formation of the oxygenated products. However, in the cases of the silyl enol ethers **1b,c** (**b**: SiR_3 = TES, **c**: SiR_3 = TBDMS) [entries 6,7], the electron transfer photooxygenations successfully occurred to give the oxygenated products together with a small amount of 1-indanone. As expected, for the silyl enol ether **1b** (SiR_3 = TES), the selective formation of α-hydroperoxy indanone **7** (57%) was observed in the reaction (the typical NMR signal, δ 10.1 ppm, of OOH). Alternatively, in the oxygenation of **1c** (SiR_3 = TBDMS), the product ratio was almost the same as in the case in the absence of MeOH [compare entry 3 with 7 in Table 1]. The dioxetane **5b** (SiR_3 = TES), which was prepared by the oxygenation with singlet oxygen,[10] did not react with MeOH under the reaction conditions (0 °C, 3 h). Thus, the reaction pathway from the dioxetane **5b** to the α-hydroperoxy ketone **7** was excluded.

In summary, we have examined the effects of the silyl group and the medium (solvent and additive) on the product ratios of the lactone **2** (from dioxetane **5**) and α-peroxy indanone **3** in the electron transfer photooxygenations of silyl enol ethers **1**. We have found, for the first time, that the oxygenation reaction can be controlled by the proper choice of the silyl group and the reaction medium. Namely, by selecting the silyl group (SiR_3 = TBDMS) and the non-nuclephilic medium (CH_2Cl_2), the preferred formation of 3-hydroxy lactone **2** was achieved. Furthermore, by adding the proper nucleophile (in this case, MeOH) in the reaction medium, the selective formation of α-peroxy indanone **7** was found when the triethylsilyl (TES) was selected for the reaction.

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