Pergamon

Tetrahedron Letters, Vol. 36, No. 23, pp. 4093-4096, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 \$9.50+0.00

0040-4039(95)00723-7

Silicon-Controlled Oxidation of Enol Acetates to Enones by Electrochemical Method

Lung Ching Lin,*[a,b] Lu Lin Chueh,[a] Shwu-Chen Tsay,[b] and Jih Ru Hwu*[b,c]

[a]Department of Chemistry, National Taiwan University,
Taipei, Taiwan 10671, Republic of China;

[b]Institute of Chemistry, Academia Sinica,
Nankang, Taipei, Taiwan 11529, Republic of China; and

[c]Department of Chemistry, National Tsing Hua University,
Hsinchu, Taiwan 30043, Republic of China

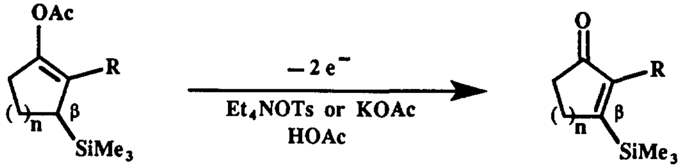
Abstract: Anodic oxidation of β-silylcycloalkanone enol acetates **1a–d** in glacial acetic acid containing tetraethylammonium *p*-toluenesulfonate afforded α,β-unsaturated β-silylcycloalkenones **2a–d** exclusively in 81–95% yields. The silyl group in **1a–d** directed the oxidation under electrochemical conditions.

Organosilyl groups have been used in control of various types of reactions involving carbocationic, carbanionic, and carboradical intermediates.[1] Their application to radical cations and radical anions is rarely investigated.[2] For example, it was reported in 1989 that silicon can direct cleavage of C–C bonds in radical cations generated by an electron impact method.[3] Whereas chemists often use electrochemical techniques to produce radical cations by anodic oxidation and radial anions by cathodic reduction. Herein we report a novel silicon-controlled anodic oxidation of β-silylcycloalkanone enol acetates to α,β-unsaturated β-silylcycloalkenones.

Shono et al.[4] found that electrochemical oxidation of 1-acetoxycyclohexene in acetic acid by using tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) as a supporting electrolyte gives a mixture of 2-cyclohexen-1-one (9%) and 2-acetoxy-1-cyclohexanone (21%). By the same method, 1-acetoxy-2-methylcyclohexene is converted to 2-methyl-2-cyclohexen-1-one exclusively in 49% yield. They also indicated that the product distributions are influenced by nature of the starting materials.[4,5] Consequently we planned to study the ability of a β $SiMe_3$ group in control of electro-oxidation reactions by using β-silylcycloalkanone enol acetates as representative examples.

We passed electricity of 2.0 F/mol at a constant current of 0.1 A (0.2 A/cm^2, terminal voltage 20 V) through glacial acetic acid (25 mL) containing β-trimethylsilyl enol acetates **1a–d** (50.0 mmol) and Et_4NOTs (50.0 mmol) at room temperature for 2 h in an undivided cell equipped with two platinum electrodes. After the starting materials were consumed, the reaction mixture was worked up with saturated aqueous $NaHCO_3$ (30 mL) and then the aqueous solution was extracted with ether. Purification of the crude products by silica gel column chromatography with a mixture of $CHCl_3$ and hexanes (1:9) as the eluant gave pure enones **2a–d** as the only products in 81–95% yields (Scheme 1 and Table 1). Performance of the electrochemical oxidations by replacement of Et_4NOTs with KOAc as the supporting electrolyte produced the same products in 53–68% yields (see Table 1).

Scheme 1



1a. n = 1, R = H
1b. n = 1, R = Me
1c. n = 2, R = H
1d. n = 2, R = Me

2a. n = 1, R = H
2b. n = 1, R = Me
2c. n = 2, R = H
2d. n = 2, R = Me

Table 1. Anodic Oxidation of β-Silyl Enol Acetates **1a–d** to Enones **2a–d** by Use of Et_4NOTs or KOAc as a Supporting Electrolyte in Acetic Acid at Room Temperature.

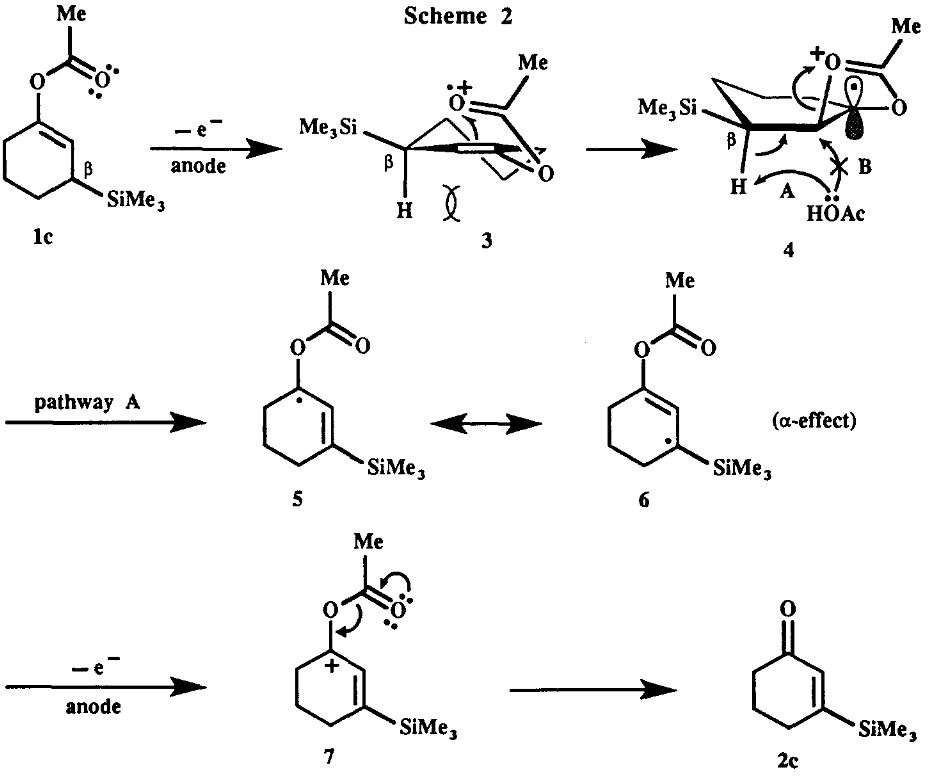
enol acetate	supporting electrolyte	product[a]	yield (%)	^{13}C NMR[b] δ (ppm)	^1H NMR[b] δ (ppm)	IR ν (cm^{-1})
1a	Et_4NOTs	2a[6]	81	−2.5, 31.6, 35.0, 141.3, 184.3, 211.6	0.18 (s), 2.30–2.67 (m), 6.30 (m)	3015, 1732, 1248
1a	KOAc	2a[6]	53			
1b	Et_4NOTs	2b	92	−2.1, 10.2, 30.0, 33.7, 148.3, 172.9, 210.7	0.04 (s), 1.63 (s), 2.11–2.40 (m)	1732, 1248
1b	KOAc	2b	64			
1c	Et_4NOTs	2c[7]	85	−2.9, 23.4, 27.6, 38.0, 135.5, 167.8, 198.6	0.09 (s), 1.90–2.37 (m), 6.17 (m)	3015, 1669, 1249
1c	KOAc	2c[7]	59			
1d	Et_4NOTs	2d	95	−0.7, 15.6, 23.6, 30.3, 38.2, 142.4, 158.5, 198.9	0.18 (s), 1.85 (s), 1.93–1.94 (m), 2.29–2.40 (m)	1661, 1246
1d	KOAc	2d	68			

[a] All of the high- and low-resolution mass spectroscopic data are satisfactory.
[b] $CDCl_3$/TMS

In comparison with the conversion of 1-acetoxycyclohexene to a mixture of 2-cyclohexen-1-one (9%) and 2-acetoxy-1-cyclohexanone (21%),[4] electrolysis of the β-silylcyclohexene **1c** produced the corresponding β-silylcyclohexenone **2c** as the only product in high yield (85%). None of 2-acetoxylated cyclohexanone derivatives were detected. In comparison with anodic oxidation of 1-acetoxy-2-methylcyclohexene to give 2-methyl-2-cyclohexen-1-one in 49% yield,[4] the efficiency can be increased dramatically to 95% yield by placement of an $SiMe_3$ group at the β position in the starting material as shown in the process **1d** → **2d**. Furthermore, under similar reaction conditions, we were able to transfer the β-silylated cyclopentanone enol acetates **1a** and **1b** to enones **2a** (81%) and **2b** (92%), respectively. These results indicate that introduction of a silyl group at the β position of 1-acetoxycycloalkenes significantly improves efficiency for the formation of 2-cycloalkenones. Moreover, the oxidation potential for β-silylcycloalkanone enol acetates **1a–d** was found ~0.4 V lower than the corresponding non-silylated species[4] (1.4–2.0 V). These results are in consistent with those reported by Koizumi, Fuchigami, and Nonaka.[2b,8]

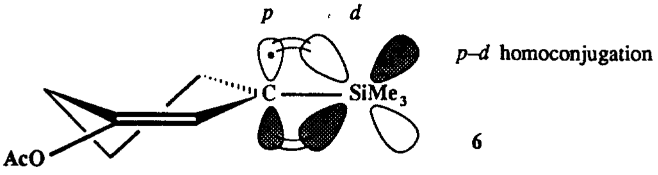
The mechanism depicted in Scheme 2, as exemplified by **1c**, can account for the results obtained from the electrochemical oxidation of β-silylcycloalkanone enol acetates. The transformation is initiated by one-electron removal from enol acetate **1c** onto the anode. The resultant radical cation **3** undergoes cyclization to produce oxonium intermediate **4**, which could be attacked by the solvent HOAc. On the basis of steric and electronic effects resulting from the $SiMe_3$ group, we believe that a β fragmentation through the pathway A is more feasible than a nucleophilic attack on an sp^3 carbon atom as shown by the pathway B: Steric congestion around the sp^3 carbon atom disfavors the pathway B to give a 2-acetoxycyclohexanone derivative. More importantly, the electronic effect resulting from the $SiMe_3$ group favors the pathway A to lead to the species represented by **5** and **6**. Barton et al.[9] reported that an $SiMe_3$ group can stabilize a carboradical by 2.6 kcal/mol. The α-stabilizing effect results from silicon "*p–d* homoconjugation"[10,11] as shown in Scheme 3. In anodic oxidation of allylsilanes, the C–Si bond is cleaved.[2,12] In contrast, the C_β–H instead of the C_β–Si bond is cleaved in the

Scheme 2



conversion of **4** → **5**. This is likely due to the C_{β}–H bond in the oxonium intermediate **4** occupying the anti-parallel position to the cleaving C–O^+ bond. Finally, one-electron oxidation occurring to **5** and **6** affords cationic species **7**, which undergoes C–O bond cleavage to give **2c**.

Scheme 3



6

In conclusion, anodic oxidation of β-silylcycloalkanone enol acetates in acetic acid containing a supporting electrolyte produced α,β-unsaturated β-silylcycloalkenones in good to excellent yields. The electrolyte can be Et_4NOTs or KOAc. This newly developed electrochemical reaction can be applied to five- and six-membered cycloalkanone enol acetates with or without a substituent at the α position. The influence resulting from an $SiMe_3$ group on carboradical cationic species can account for the formation of α,β-unsaturated cycloalkenones as the exclusive products.

Acknowledgement: For financial support, we are indebted to the National Science Council of Republic of China (Grant NSC-84-2113-M007-004) and to Academia Sinica. We are grateful to the reviewer for his valuable suggestions. J. R. Hwu is honored as "The Outstanding Young Persons of the World for 1994" in the category of Scientific and Technological Development.

REFERENCES AND NOTES

1. See the following representative articles and references cited therein: (a) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*, Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 14; (b) Hwu, J. R.; Wetzel, J. M.; Lee, J. S.; Butcher, R. J. *J. Organomet. Chem.* **1993**, *453*, 21; (c) Hwu, J. R.; Chen, C. N.; Shiao, S.-S. *J. Org. Chem.* **1995**, *60*, 856.
2. For examples, see: (a) Yoshida, J.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 3373; (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 219.
3. Furth, P. S.; Hwu, J. R. *J. Org. Chem.* **1989**, *54*, 3404.
4. Shono, T.; Matsumura, Y.; Nakagawa, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3532.
5. Shono, T.; Okawa, M.; Nishiguchi, I. *J. Am. Chem. Soc.* **1975**, *97*, 6144.
6. Reuter, J. M.; Sinha, A.; Salomon, R. G. *J. Org. Chem.* **1978**, *43*, 2438.
7. Otera, J.; Mandai, T.; Shiba, M.; Saito, T.; Shimohata, K.; Takamori, K.; Kawasaki, Y. *Organometallics* **1983**, *2*, 332.
8. Also see: Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544.
9. Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Ravis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644.
10. Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6715.
11. Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.
12. (a) Schäfer, H.; Hermeling, D.; Lange, K. H. Spring Meeting of the Electrochemical Society, Cincinnati, Ohio, Extended Abstracts, **1984**, 441; (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Chem. Express* **1986**, *1*, 355; (c) Yoshida, J.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 211.

(*Received in Japan* 30 *January* 1995; *revised* 22 *March* 1995; *accepted* 12 *April* 1995)