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β-Effects of Silicon in Directing Fragmentation of *β*-Silylcycloalkanone Radical Cations

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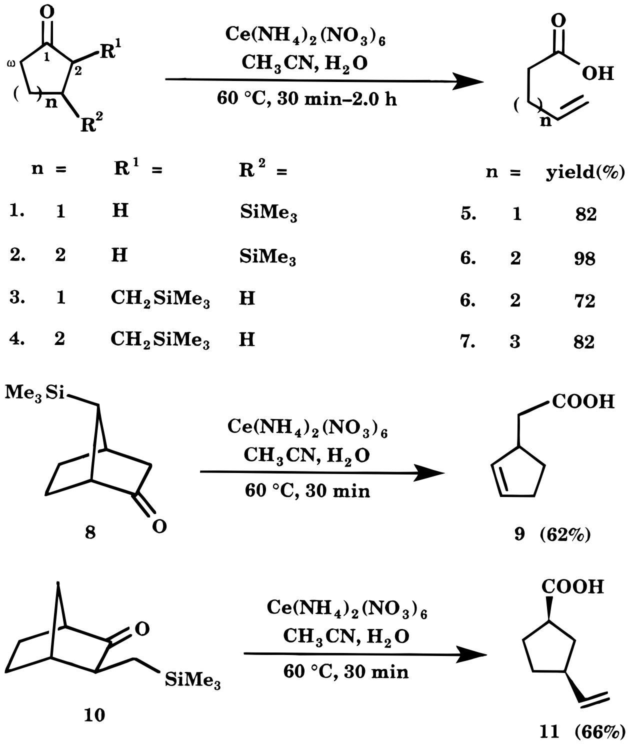
Silicon can direct the Norrish type I cleavage of *β*-(trimethylsilyl)cycloalkanones at the C_1-C_2 bond in a highly regioselective manner.[1] This photochemical reaction has been applied in organic synthesis.[2−4] Carboradical intermediates generated therein are stabilized by a *β*-silyl group predominantly through "$\sigma-\pi$ hyperconjugation".[5−8]

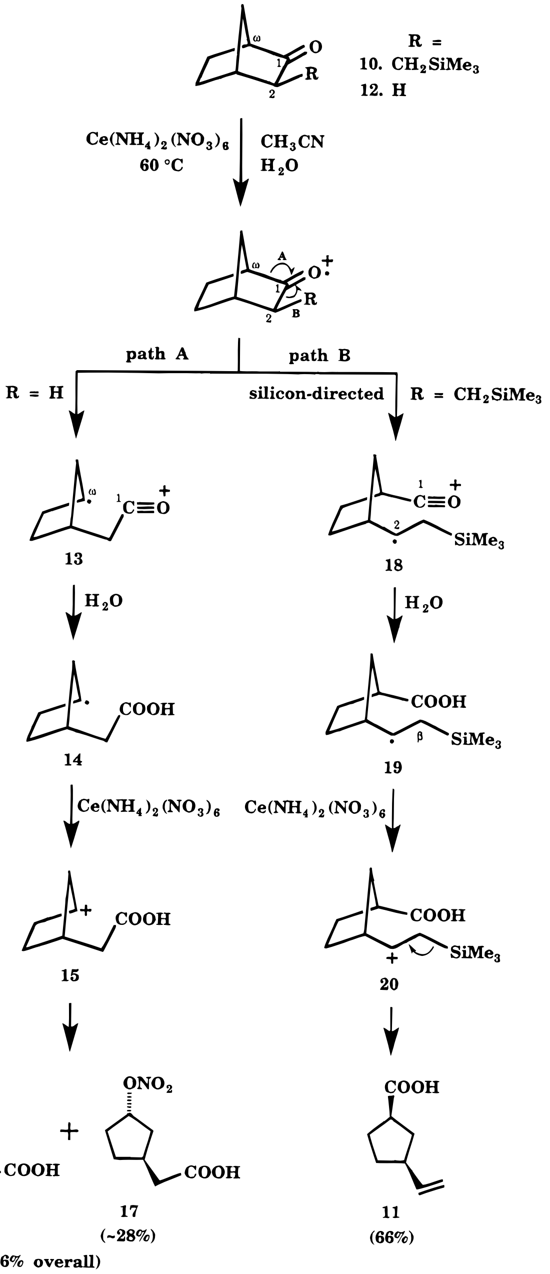
We planned to explore the possibility of using silicon to direct chemical processes involving radical cationic intermediates generated from cycloalkanones. An ideal outcome would lead us to obtain a single product bearing synthetically valuable functionalities, instead of a mixture containing an ester and an alkenyl aldehyde generated through the Norrish type I cleavage.[1] Herein we report a new silicon-directed fragmentation as shown in Scheme 1, in which the highly regioselective cleavage of the C_1-C_2 bond in *β*-(trimethylsilyl)cycloalkanones occurred by use of ceric ammonium nitrate (CAN) to give the desilylated *ω*-alkenylcarboxylic acids.

Scheme 1



	n =	R1 =	R2 =		n =	yield(%)
1.	1	H	$SiMe_3$	5.	1	82
2.	2	H	$SiMe_3$	6.	2	98
3.	1	CH_2SiMe_3	H	6.	2	72
4.	2	CH_2SiMe_3	H	7.	3	82

Scheme 2



One-electron oxidation of a carbonyl group to give the corresponding radical cation can be accomplished by use of CAN.[9,10] Thus, we treated a 50% aqueous acetonitrile solution (20 mL) containing a *β*-(trimethylsilyl)cycloalkanone (2.0 mmol, 0.10 M) and CAN (2.4 equiv) at various temperatures between 25 and 82 °C. The optimal conditions were found at 60 °C. Within 2.0 h, the solution turned from dark brown to pale yellow or colorless at 60 °C. Change of the color indicated completion of the reactions. Workup followed by chromatographic purification afforded *ω*-alkenylcarboxylic acids in 62−98% yields (Scheme 1). There was no byproduct detected through the C_1-C_ω bond cleavage.

This new reaction was applicable to five- and six-membered cycloalkanones bearing a *β* silyl group at an endo (i.e., **1** and **2**) or an exo (i.e., **3** and **4**) position. Furthermore, the silicon-directed fragmentation was successfully extended to bicyclic ketones **8**

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and **10**. The desired products **9** and **11** were obtained in 62 and 66% yields, respectively.

Deslongchamps et al.[11] reported results from the oxidation of nonsilylated bicyclic ketone **12** by CAN in wet acetonitrile. A mixture of *cis*- and *trans*-cyclonitratocarboxylic acids **16** and **17** was generated in a 46% overall yield after 1.5 h (Scheme 2). The oxidative cleavage occurs at the C_1-C_ω bond, which is marked in the nonsilylated ketone **12**. The regioselective cleavage of the C_1-C_ω bond likely comes from the generation of the thermodynamically more stable secondary carboradicals **13** and **14** as well as the carbocation **15** instead of the less stable primary species resulting from cleavage of the C_1-C_2 bond. Under the same conditions, we converted β-silyl bicyclic ketone **10**, through cleavage of the C_1-C_2 bond therein, to alkenylcarboxylic acid **11** in 66% yield. Cleavage of either the C_1-C_2 or the C_1-C_ω bond in **10** would lead to a secondary carboradical. Nevertheless, the silyl group at the β-position toward the carboradical centers in **18** and **19** as well as the carbocationic center in **20** exerts an additional stabilizing effect. The positive charge and the radical, however, may be switched in the oxygen and carbon centers in **18**; such a radical cationic intermediate would lead to the same product **11**. As a result, silicon plays a vital role on the regioselective fragmentation of β-silyl ketones.

In addition to silicon, the β-effect of tin has also been applied to direct organic reactions;[12,13] examples include the C−C bond fragmentations in the Baeyer−Villiger reaction and the Beckman reaction.[14] We planned to realize the diversity of the electronic effects of these two elements in group IV. Subsequently, 3-(tri-*n*-butyl)stannylcyclopentan-1-one was treated with CAN in wet acetonitrile at 60 °C. We found that destannylation took place to afford 2-cyclopenten-1-one in 81% yield. Furthermore, we performed the destannylation on 3-(tri-*n*-butyl)stannylcyclohexan-1-one with CAN at 60 °C to give 2-cyclohexen-1-one in 85% yield. These successful conversions offer a new method by use of a stannyl moiety as a “protective group”. Thus, cycloalkanones bearing a β-silyl or -stannyl group gave an entirely different class of products upon exposure to CAN under the same conditions.

In conclusion, silicon can direct the C−C bond cleavage in β-silylcycloalkanones in a highly regioselective manner by use of CAN. A single product, ω-alkenylcarboxylic acid, was produced in good to excellent yields under mild conditions. In comparison with the Norrish type I cleavage, this reaction may have a greater potential in organic synthesis.

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Supporting Information Available: Synthetic procedures and spectroscopic data for **5**−**11**, **23**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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