Acknowledgment. The authors are grateful to the Research Corporation for financial support. We wish to thank Professor Glen A. Russell for carrying out the MO calculation on **3a**$\cdot^-$.

Registry No.—**3a**, 10474-58-4; **3a**$\cdot^-$, 58873-29-3.

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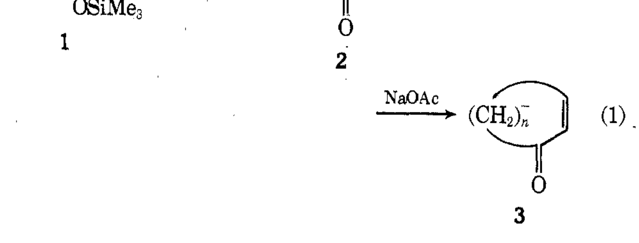
Communications

Reaction of 1-Silyloxybicyclo[*n*.1.0]alkanes with $Fe^{III}Cl_3$. A Facile Synthesis of 2-Cycloalkenones via Ring Enlargement of Cyclic Ketones

Summary: Reactions of 1-trimethylsilyloxybicyclo[*n*.1.0]alkanes (**1**) with $Fe^{III}Cl_3$, followed by treatment with sodium acetate in methanol, furnish 2-cycloalkenones (**3**) in high yields; similar reactions with bis(trimethylsilyloxy)bicyclo[*n*.1.0]alkanes (**4**) afford cycloalkane-1,3-dione (**5**) in moderate yields.

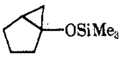
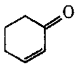
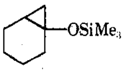
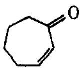
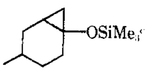
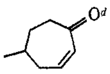
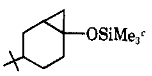
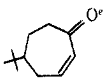
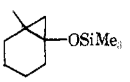
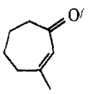
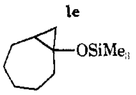
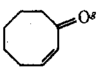
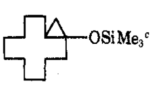
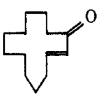
Sir: Much attention has been directed to the utilization of silyl groups in organic synthesis in the past several years.[1] In our previous paper,[2] we described a regiospecific formation of 1,4 diketones by the oxidative coupling of silyl enol ethers with Ag_2O, in which we assumed Ag^I enolate intermediate regiospecifically formed through the reaction of silyl enol ether with Ag_2O. Herein, we wish to report an oxidation reaction of 1-silyloxybicyclo[*n*.1.0]alkanes (**1**) with $Fe^{III}Cl_3$, leading to the formation of the corresponding 2-cycloalkenone (**3**) via 3-chlorocycloalkanone (**2**) in moderate to excellent yields according to the eq 1. This reaction presents a new method for one-carbon ring homologation of cycloalkanones. It is of practical use since 1-silyloxybicyclo[*n*.1.0]alkanes are readily prepared by the Simmons–Smith reaction of silyl enol ethers of cycloalkanones.[3] Recently, Stork has reported a comparable ring homologation of cycloalkanones by the dichlorocyclopropanation of silyl enol ether followed by hydrolysis.[4]



A typical experimental procedure is illustrated by the reaction of 1-trimethylsilyloxybicyclo[4.1.0]heptane (**1b**) with $Fe^{III}Cl_3$. To a stirred solution of anhydrous $Fe^{III}Cl_3$ (973 mg, 6 mmol) in dimethylformamide (4 ml), a solution of **1b** (368 mg, 2 mmol) and pyridine (158 mg, 2 mmol) in dimethylformamide (4 ml) was added dropwise over 2 h at 0 ~ 10 °C under nitrogen. The resultant brown solution was stirred at room temperature for 1 h, and then poured into cold 1 N HCl aqueous solution and extracted repeatedly with chloroform. The chloroform extract was successively washed with 1 N HCl aqueous solution and with brine, dried over $MgSO_4$ and concentrated in vacuo. The concentrate was subjected to preparative GLC to afford 3-chlorocycloheptanone (**2b**) in 93% yield: ir 1705 cm^{-1}; NMR (CCl_4 with TMS) δ 1.4 ~ 2.3 (m, 6 H), 2.3 ~ 2.6 (m, 4 H), 4.1 ~ 4.4 (m, 1 H); mass M^+ 146 and 148 (3:1). After the concentrate was refluxed with sodium acetate in methanol for 2 h, 2-cycloheptenone (**3b**) was isolated in 84% yield by preparative GLC, which was identical in all respects with an authentic sample. No C_7 cyclic ketones other than **3b** were detected in the reaction mixture by GLC. Some results of 2-cycloalkenone synthesis are summarized in Table I.

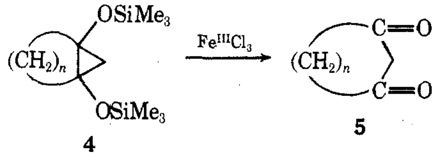
Some remarks are to be added to Table I. The reaction of 1-trimethylsilyloxybicyclo[3.1.0]hexane (**1a**) with $Fe^{III}Cl_3$ at 0 ~ 10 °C produced 2-cyclohexenone (**3a**)[5] in almost quantitative yield prior to the treatment with sodium acetate in methanol. In this case, 3-chlorocyclohexanone (**2a**) initially formed underwent readily dehydrochlorination under the reaction conditions. The reaction with 1-trimethylsilyloxy-6-methylbicyclo[4.1.0]heptane (**1e**) afforded 3-methyl-2-cycloheptenone (62% isolated yield), after the treatment with sodium acetate, which was not contaminated with any isomeric methylcycloheptenones. This reaction represents a transformation of unsymmetrical cycloalkanone into regiospecifically homologated 2-cycloalkenone. The reaction of 1-trimethylsilyloxybicyclo[10.1.0]tridecane (**1g**) with $Fe^{III}Cl_3$, which was very sluggish at 0 ~ 10 °C, was carried out by heating at 80 °C for 3 h. Oxidative cleavage of the carbon–carbon bond of **1g** and dehydrochlorination of the resulting 3-chlorotridecanone (**2g**) took place successively in one flask at a temperature of 80 °C.[6] The product of *trans*-2-cyclotridecenone (**3g**) was isolated in 81% yield by preparative TLC on silica gel: ir 1690, 1662, 1625 cm^{-1}; NMR (CCl_4 with TMS) δ 1.15 ~ 1.85 (m, 16 H), 2.10 ~ 2.50 (m, 4 H), 6.05 (d, 1 H, J = 15.6 Hz), 6.61 (td, 1 H, J = 15.6 and 7.0 Hz); mass M^+ 194. Use of diethyl ether solvent[7] in the ring enlargement reaction resulted in a remarkable reduction in the yield of the corresponding 2-cycloalkenone [e.g., 5-methyl-2-cycloheptenone (47%), *trans*-2-cyclotridecenone (56%)]. $CuCl_2$ can also be used in place of $Fe^{III}Cl_3$ in the present reaction, but was less effective [e.g., 2-cyclohexenone (60% yield)] than $Fe^{III}Cl_3$.

Table I. Synthesis of 2-Cycloalkenone

No.	1-Silyloxybicyclo-[*n*.1.0]alkane	2-Cycloalkenone[a] (yield, %)[b]
1	 **1a**	 **3a** (98)
2	 **1b**	 **3b** (84)
3	 **1c**	 **3c** (97)
4	 **1d**	 **3d** (70)
5	 **1e**	 **3e** (62)
6	 **1f**	 **3f** (92)
7	 **1g**	 **3g** (81)

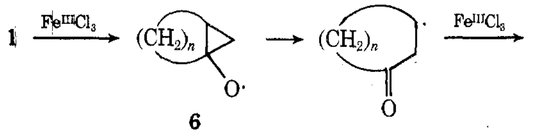
[a] Satisfactory microanalysis data were obtained for all new compounds. [b] No attempt has been made to optimize the reaction conditions. [c] Cis–trans mixture, as judged by NMR. [d] An axial–equatorial mixture. **3c**: ir 1665 cm^{-1}; NMR (CCl_4 with TMS) δ 1.05 and 1.08 (two d, 3 H, J = 6.0 Hz), 1.5~2.1 (m, 3 H), 2.1~2.5^4 (m, 4 H), 5.84 (br d, 1 H, J = 12.0 Hz), 6.40 (m, 1 H). [e] An axial–equatorial mixture. **3d**: ir 1665 cm^{-1}; NMR (CCl_4 with TMS) δ 0.90 and 0.95 (two s, 9 H), 1.2~2.6 (m, 7 H), 5.80 (br d, 1 H, J = 12.0 Hz), 6.43 (m, 1 H). [f] **3e**: ir 1650 cm^{-1}; NMR (CCl_4 with TMS) δ 1.97 (s, 3 H), 1.7~2.0 (m, 4 H), 2.3~2.7 (m, 4 H), 5.85 (broad s, 1 H). [g] **3f**: ir 1660 cm^{-1}; NMR (CCl_4 with TMS) δ 1.4~2.2 (m, 6 H), 2.3~2.7 (m, 4 H), 5.81 (d, 1 H, J = 12.0 Hz), 6.14 (td, 1 H, J = 12.0 and 6.0 Hz).

The present procedure for one-carbon ring homologation of cyclic ketone is also applicable to bis(trimethylsilyloxy)bicyclo[*n*.1.0]alkanes (**4**) which are prepared by the cyclopropanation of bis(silyloxy)enediol derived from the silyl-acyloin synthesis.[8] This reaction provides a new route to cycloalkane-1,3-diones (**5**, eq 2) [e.g., cycloheptane-1,3-dione (68%), cyclonane-1,3-dione (72% yield)].



4 **5** (2)

The reaction for one-carbon homologation of cycloalkanones in this study is mechanistically interesting in terms of the regioselectivity in the ring-opening of silyloxybicyclo[*n*.1.0]alkane (**1** and **4**), of which the bridging bond is cleaved. This is contrasted with the bromination[9] and the potassium *tert*-butoxide treatment[10] of 1-silyloxybicyclo[*n*.1.0]alkanes producing 2-bromomethylcycloalkanones and 2-methylcycloalkanones, respectively. Based upon the extensive studies on the reaction of cyclopropanol with various halogenating reagents by DePuy and coworkers,[7] the present ring enlargement reaction may be well explained by a mechanism involving an alkoxy radical intermediate (**6**) which undergoes the homolytic β scission of the bridging carbon–carbon bond, and the subsequent abstraction of chlorine by the resulting carbon radical species (**7**) to give 3-chlorocycloalkanone (**2**) (eq 3). Detailed understanding of the reaction mechanism must await further study.



6 **7** (3)

Ring enlargement of the related silyloxybicycloalkanes is now being carried out in this laboratory.

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(5) Identical in all respects with an authentic sample.

(6) The 2-cycloalkenone synthesis in this study can be also performed in one flask by heating the reaction mixture of **1**, pyridine, and $Fe^{III}Cl_3$ in DMF at 80 °C, but in decreased yields [for example, 5-methyl-2-cycloheptenone (**3c**) (65% yield)].

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Yoshihiko Ito, Syotaro Fujii, Takeo Saegusa*
Department of Synthetic Chemistry
Kyoto University, Kyoto, Japan

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