the case of 2-bromooctane, representative results are indicated in Table V.

The procedures we describe here are milder, more efficient, less expensive and more convenient (smaller reaction times, lower temperatures, easier workup) than those published previously. The stereo- and regioselectivities obtained are very close to those observed with alkoxide in alcohol at reflux.

These results contitute a new illustration of the potential in organic synthesis of reactions performed under solid–liquid PTC conditions in the absence of solvent.

Registry No. 2-Bromooctane, 557-35-7.

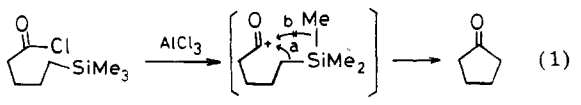
Communications

A Cyclopentanone Annulation via Intramolecular Acylation of Alkylsilanes

Summary: A facile construction of cyclopentanones is achieved via a ring closure of 5-(trimethylsilyl)alkanoyl chlorides under the influence of $AlCl_3$.

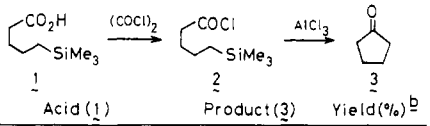
Sir: Cyclopentanones are widely found in naturally occurring products, and exploration of new procedures for construction of such frameworks from readily available acyclic precursors is still required in natural product synthesis. Among the many approaches, a ring closure by the combination of the acyl cation and the alkyl anion equivalent would be one of the most straightforward methodologies (Scheme I).

To effect this transformation, the alkyl anion equivalent depicted in Scheme I should be compatible with the nucleophilic carbonyl functionality in the same molecule. For such purposes, silicon-substituted alkyl groups seem to be employed as the incipient anion because the carbon–silicon bond is weakly polarized to fulfill the above requirement. Although the utility of unsaturated organosilicon compounds such as alkenyl-, allyl-, and arylsilanes has been amply demonstrated,[1] synthetic reactions dealing with simple alkyl-silicon bonds have not been elucidated up to now.[2] Since alkylsilanes are considerably stable under various circumstances, their reactions are alluded to require drastic conditions. Selective transfer of an alkyl group from an alkyltrimethylsilane is also quite problematic. However, we disclose here that Lewis acid mediated intramolecular acylation of alkylsilanes[3,4] works quite well for the preparation of a variety of cyclopentanones. The reaction proceeds via a selective fission of an appropriate carbon–silicon bond to yield the corresponding cyclopentanone (eq 1).

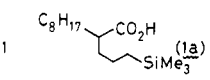
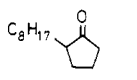
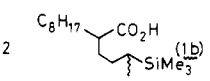
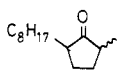
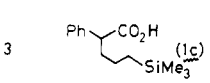
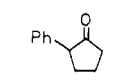
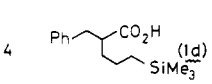
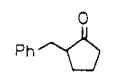
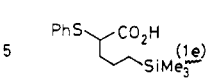
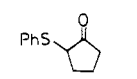
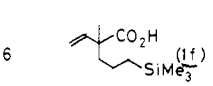
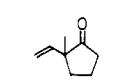
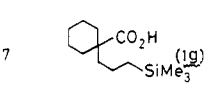
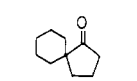


(1)

Table I. Cyclopentanone Synthesis by Intramolecular Acylation of 5-(Trimethylsilyl)alkanoyl Chlorides[a]



1 2 3

Run	Acid (1)	Product (3)	Yield (%)[b]
1			87 (92)[c]
2			83
3			84
4			85
5			60[d]
6			67[e]
7			70

[a] Reactions are carried out in 0.2–0.3-mmol scale with the reactant ratio $1/(COCl)_2/AlCl_3 = 1:2:1$. [b] Overall yield from 1. Products are isolated by chromatography. [c] Reaction in 3.5-mmol scale and the product was isolated by Kugelrohr distillation. [d] Reactant ratio: $1/(COCl)_2/AlCl_3 = 1:1.5:0.75$. [e] Relatively low yield may reflect the volatility of the product.

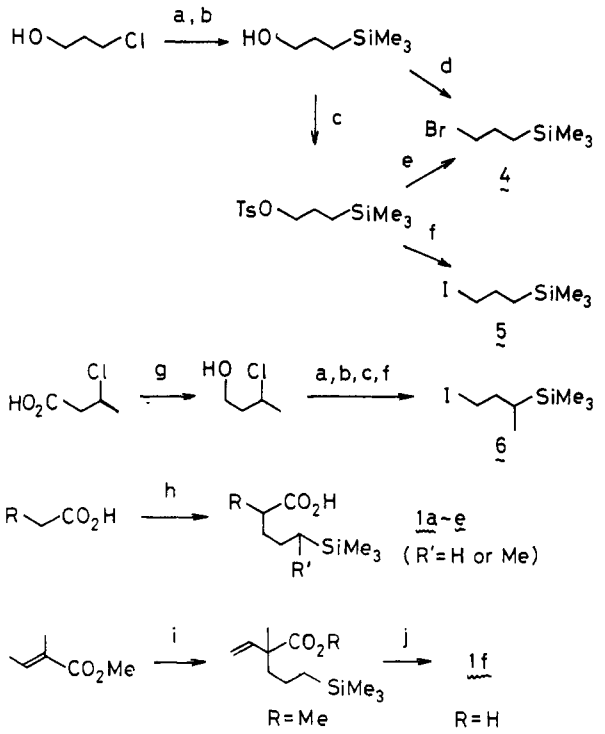
The starting materials are readily obtained by standard methods (Scheme II). Alkylation of the dianion of carboxylic acid[5] with 3-(trimethylsilyl)alkyl bromide or iodide is a most convenient method to prepare 5-(trimethylsilyl)alkanoic acids. In others case where carboxylic acids cannot be employed (e.g., run 6), alkylation of an ester with the halide followed by hydrolysis is an alternative way.

(1) (a) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981. (b) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.
(2) Reference 1b, pp 159–162.
(3) On intermolecular acylation of tetraalkylsilanes: Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493. Olah, G. A.; Ho, T.-L.; Prakash, G. K. S.; Gupta, B. G. B. *Synthesis* **1977**, 677.
(4) On intramolecular acylation of vinylsilanes: Burke, S. D.; Murtiashaw, C. W.; Dike, M. S.; Strickland, S. M. S.; Saunders, J. O. *J. Org. Chem.* **1981**, *46*, 2400. Nakamura, E.; Fukuzaki, K.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1983**, 499. Mikami, K.; Kishi, N.; Nakai, T. *Tetrahedron Lett.* **1983**, *24*, 795.
(5) Pfeffer, P. E.; Silbert, L. S.; Chirinko, J. M., Jr. *J. Org. Chem.* **1972**, *37*, 451.
(6) Cahiez, G.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1978**, 3013.
(7) Sommer, L. H.; Van Strien, R. E.; Whitemore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056.
(8) Herrmann, J. L.; Kieczykowsky, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2433.

0022-3263/84/1949-1140$01.50/0

Scheme I

Scheme II



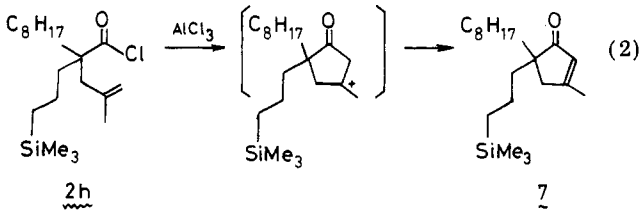
[a] Reference 6. [b] Me_3SiCl. [c] *p*-TsCl, pyridine. [d] PBr_3 (ref 7). [e] LiBr, DME, reflux. [f] NaI, acetone. [g] $LiAlH_4$, Et_2O. [h] LDA-HMPA, THF (ref 5), **4**, **5**, or **6**. [i] LDA-HMPA, THF (ref 8); **5**. [j] LiI (7 equiv), collidine (1 equiv), DMF, 140 °C.

The conversion of the acids to the corresponding acid chlorides is performed by treatment with oxalyl chloride in benzene.[9] After removal of excess oxalyl chloride and the solvent in vacuo, the residual crude acyl chlorides are used directly for the cyclization. The results are summarized in Table I.

Treatment of the acid chloride **2** with an equimolar amount of $AlCl_3$ in methylene chloride at room temperature gave the expected cyclopentanone cleanly.[10,11] ^1H NMR analysis of the crude product revealed that the formation of the methyl ketone is practically excluded. Thus intramolecular delivery of the proper alkyl group bearing the trimethylsilyl group (path a in eq 1) is far more favorable than the inter- or intramolecular migration of the methyl group. Of the Lewis acids examined, $AlCl_3$ is proved to be the most effective. Neither $TiCl_4$ nor $BF_3{\cdot}OEt_2$ effects this cyclization so efficiently.

The reaction is not limited to a substrate including primary alkyl moiety. A *sec*-alkyltrimethylsilane (**1b**) is also employable equally well (run 2) to yield the corresponding α,α'-disubstituted cyclopentanone.

Since this cyclization is performed in the presence of a Lewis acid, the question may arise as to whether an electrophilic functional group survives the reaction conditions. In order to clarify this point, the cyclization has also been examined on substrates having an aromatic ring and an olefinic linkage at a suitable position close to the reaction center. As shown in Table I, the cyclization can be effected cleanly with the substrates bearing $\Delta^{3,4}$-double bond, which leads to the formation of 2-aryl- and 2-vinylcyclopentanones (runs 3 and 6). Further, a $\Delta^{4,5}$-double bond incorporated in a benzene ring, which is very susceptible to the intramolecular Friedel–Crafts acylation,[12] does not block the present cyclization (run 4). Even in the presence of a more electrophilic phenylthio group (run 5), the product yield still falls in an acceptable range. However, in contrast to an aromatic ring, the cyclization of the 2-methallyl-5-(trimethylsilyl)alkanoyl chloride (**2h**) took place at the methallyl site to yield the cyclopentenone **7** as a major product (eq 2). Stability of the resulting *tert*-alkyl cation may account for this course of the reaction.[4]



(2)

These results clearly show that the present cyclization is of general use for cyclopentanone annulation. Another important feature is that alkylsilanes, which are usually quite stable during several synthetic operations, can be utilized for selective carbon–carbon bond formation under appropriate reaction conditions.

Further studies on synthetic application are now in progress.

Acknowledgment. This work is supported by a grant from the Ministry of Education, Science, and Culture of the Japanese Government.

Registry No. **1a**, 88729-67-3; **1b**, 88729-68-4; **1c**, 88729-69-5; **1d**, 88729-70-8; **1e**, 88729-71-9; **1f**, 88729-72-0; **1g**, 88729-73-1; **2h**, 88729-74-2; **3a**, 40566-23-2; **3b**, 88729-75-3; **3c**, 1198-34-1; **3d**, 2867-63-2; **3e**, 52190-40-6; **3f**, 88729-76-4; **3g**, 4728-91-0; **4**, 10545-34-3; **5**, 18135-48-3; **6**, 88729-79-7; **7**, 88729-77-5; 3-chloropropan-1-ol, 627-30-5; 3-(trimethylsilyl)propan-1-ol, 2917-47-7; 3-(trimethylsilyl)propan-1-ol tosylate, 88729-78-6; 3-chlorobutanoic acid, 1951-12-8; 3-chlorobutan-1-ol, 2203-35-2; decanoic acid, 334-48-5; benzeneacetic acid, 103-82-2; benzenepropanoic acid, 501-52-0; (phenylthio)acetic acid, 103-04-8; methyl 2-methyl-2-butenoate, 41725-90-0; methyl 2-[3-(trimethylsilyl)propyl]-2-methyl-3-butenoate, 88729-80-0.

(9) Adams, R.; Ulich, L. H. *J. Am. Chem. Soc.* **1920**, *42*, 599.

(10) A typical procedure is as follows. 2-(3-(Trimethylsilyl)propyl)-decanoic acid (1.00 g, 3.50 mmol) was treated with oxalyl chloride (0.6 mL, 7 mmol) in benzene (10 mL) at 70 °C for 30 min under nitrogen. Then the excess oxalyl chloride was removed together with benzene in vacuo at room temperature. The resulting crude acyl chloride was dissolved in methylene chloride (14 mL) and was added dropwise to a suspension of $AlCl_3$ in methylene chloride (6 mL) at 0 °C under nitrogen. The mixture was stirred for 2 h at room temperature and then quenched with dilute HCl. From the combined ethereal extracts, 2-octylcyclopentanone (0.63 g, 92%) was obtained by Kugelrohr distillation.

(11) In contrast to the cyclopentanones, attempts for cyclobutanone and cyclohexanone annulation usually resulted in the formation of complex mixtures.

(12) Johnson, W. S. *Org. React.* (*N.Y.*) **1944**, *2*, 114.

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