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Facile Construction of a Tricyclo[5.3.0.0^{1,4}]decenone Ring System by the Brook Rearrangement-Mediated [3 + 4] Annulation

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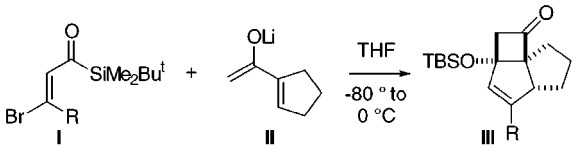
ABSTRACT

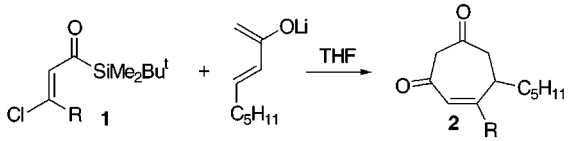


Reaction of 3-alkyl-3-haloacryloylsilanes I with the lithium enolate of 1-acetyl-1-cyclopentene II afforded tricyclo[5.3.0.0^{1,4}]decenone derivatives III via Brook rearrangement-mediated [3 + 4] annulation.

Recently, we have reported that the reaction of β,β-dichloroacryloylsilane with ketone enolates proceeds smoothly at lower temperatures to afford 3-alkyl-3-chloro-4-hydroxy-2-cyclopentenone derivatives via Brook rearrangement-mediated [3 + 2] annulation followed by dechlorosilylation.[1,2] Herein, we describe the direct formation of tricyclo[5.3.0.0^{1,4}]-decenone ring system from the reaction of β-alkyl-β-haloacryloylsilane with the lithium enolate of 1-acetyl-1-cyclopentene, which was found during an extension of the [3 + 2] annulation for the formation of cycloheptenedione derivatives by the [3 + 4] annulation[3] using enolates of alkenyl methyl ketones.

Our initial attempt to react β-chloro-β-methylacryloylsilane **1a**[4] with the lithium enolate of 3-nonen-2-one produced the corresponding [3 + 4] annulation−dechlorosilylation product **2a** in 75% yield (Scheme 1). Additional examples using acyclic enone enolates are given in Scheme 1.

Scheme 1



	R	conditions	yield (%)
a	CH_3	-80 ° to 0 °C	75
b	*n*-Bu	-80 ° to 0 °C	41
c	*n*-hexyl	-80 ° to 0 °C	33
d	*t*-Bu	rt	54

In sharp contrast to these results, reaction of **1** with the enolate of 1-acetyl-1-cyclopentene (**3**) produced tricyclo-

(1) Takeda, K.; Ohtani, Y.; Ando, E.; Fujimoto, K.; Yoshii, E.; Koizumi, T. *Chem. Lett*. **1998**, 1157−1158.

(2) For the [3 + 2] annulation, see: (a) Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc*. **1993**, *115*, 9351−9352. (b) Takeda, K.; Nakayama, I.; Yoshii, E. *Synlett* **1994**, 178−178. (c) Takeda, K.; Kitagawa, K.; Nakayama, I.; Yoshii. E. *Synlett* **1997**, 255−256.

(3) (a) Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc*. **1995**, *117*, 6400−6401. (b) Takeda, K.; Nakajima, A.; Yoshii, E. *Synlett* **1996**, 753−754. (c) Takeda, K.; Nakajima, A.; Takeda, M.; Okamoto, Y.; Sato, T.; Yoshii, E.; Koizumi, T.; Shiro, M. *J. Am. Chem. Soc*. **1998**, *120*, 4947−4959. (d) Takeda, K.; Nakajima, A.; Takeda, M.; Yoshii, E. *Org. Synth*. **1999**, *76*, 199−213.

(4) (a) Cunico, R. F.; Zhang, C. *Tetrahedron Lett*. **1992**, *33*, 6751−6754. (b) Cunico, R. F.; Zhang, C. *Tetrahedron* **1995**, *51*, 9823−9838.

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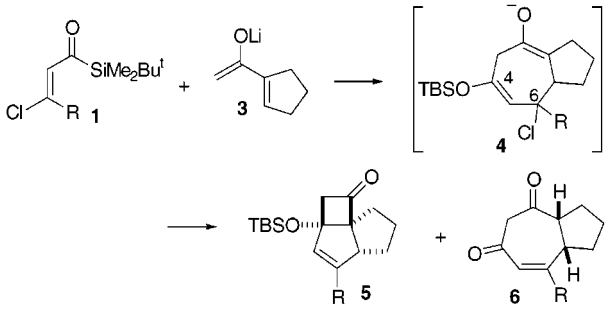
[5.3.0.0^{1,4}]decenone derivatives **5**[5] in yields dependent upon the β-substituent of **1**, in addition to **6**, a [3 + 4] annulation−dechlorosilylation product (Scheme 2). The formation of **5**

Scheme 2



	R	conditions	yield (%) 5	6
a	CH_3	-80 ° to 0 °C	25	35
b	*n*-Bu	-80 ° to 0 °C	48	11
c	*n*-hexyl	-80 ° to 0 °C	22	31
d	*t*-Bu	rt	4	43

can be understood in terms of an S_N'-like intramolecular attack of the enolate at C-4 position in the intermediate **4**.

In the reactions with enolates of 1-acetyl-1-cyclohexene, **7** was the only product except for R = *t*-Bu where the corresponding tricyclic compound **8d** was obtained in 9% yield (50% yield of **7d**) (Figure 1).

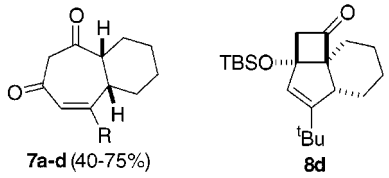
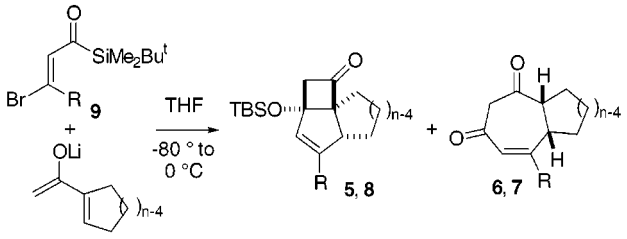


Figure 1.

These results suggest that small structural changes in **1** and the enolates significantly affect the product distributions and led us to consider replacing the chlorine atom with a better leaving group. When the β-bromo derivative **9**[4] was reacted with **3** under the same conditions as those for the β-chloroderivative **1** (Scheme 3), **5** was obtained as a sole product in all cases except for **9d** (R = *t*-Bu) where 7% of **6** was isolated. The same reaction with the enolate of 1-acetylcyclohexene afforded the corresponding tricyclic compounds **8** in moderate yield, in sharp contrast to the reaction with **1** in which only substrate **1d** afforded a tricyclic product (**8d**).

(5) The structures were assigned on the basis of their IR spectra, which showed a peak at 1775 cm^{-1}, and confirmed by a X-ray analysis of **5a** after derivatization.

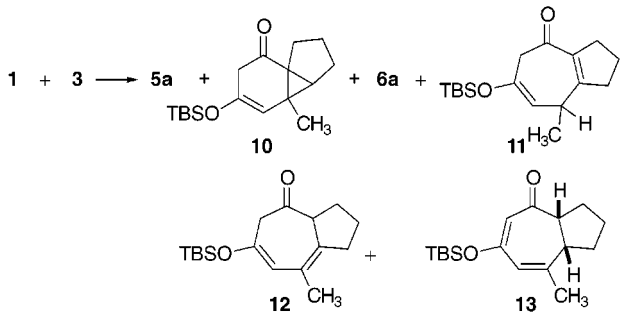
Scheme 3



	R	yield (%), n = 5 5	6	yield (%), n = 6 8	7
a	CH_3	68	0	27	45
b	*n*-Bu	49	0	27	14
c	*n*-hexyl	41	0	35	17
d	*t*-Bu	51	7	58	14
e	*c*-C_3H_5	56	0	39	32

A low-temperature quenching experiment was carried out using **1a** to gain information on the reaction path for the formation of the tricyclic compound **5** and the cycloheptenedione **6** (Scheme 4). Tricyclic compound **10**,[6] an intramolecular alkylation product of the enolate at C-6 position in **4**, and **11** and its double bond isomers **12** and **13** were isolated. The yield of **6a** increased at the expense of **10** with rising temperature, whereas that of **5a** was relatively constant, suggesting that the major pathway involves the initial formation of **5a** and **10** by way of intramolecular alkylation of the enolate in **4** followed by transformation of **10** to **6a** via **11**−**13**. In fact, to duplicate the conditions present when LDA was used to generate the enolates, treatment of **10** with LiCl and diisopropylamine in THF at −80 ° to 0 °C afforded **6a** (56%) and **13** (14%), while in the case of **5a**, no reactions occurred under the same conditions.

Scheme 4



conditions	yield (%) 5a	10	6a	11	12	13	1
-80 °C, 1h	3	5	0	3	0	0	59
-80 ° to -50 °C	22	14	12	3	4	0	20
-80 ° to -30 °C	21	1	15	2	6	23	12
-80 ° to -15 °C	27	0	43	5	0	3	3

(6) The structure of **10** was assigned on the basis of its ^{13}C NMR spectrum that shows peaks assigned as a quatanary carbon at 34.2 and 49.7 ppm and on the basis of its IR absorption at 1685 cm^{-1} which is indicative of the cyclopropyl carbonyl moiety with an siloxyvinyl group, see: Lyle, T. A.; Frei, B. *Helv. Chim. Acta* **1981**, *64*, 2598−2605.

In conclusion, we have developed a rapid and efficient route for the synthesis of a tricyclo[5.3.0.$0^{1,4}$]decenone ring system, which is a potentially useful intermediate for synthesizing a variety of biologically significant compounds, but which is difficult to make by other approaches.[7]

(7) For preparation of tricyclo[5.3.0.$0^{1,4}$]decenone ring system using α-oxycyclopropylcarbinol-cyclobutanone rearrangement, see: (a) Wenkert, E.; Arrhenius, T. S. *J. Am. Chem. Soc*. **1983**, *105*, 2030−2033. For preparation by photochemical reaction, see: (b) Exon, C.; Nobbs, M.; Magnus, P. *Tetrahedron* **1981**, *37*, 4515−4519, (c) Wiesner, K. *Tetrahedron* **1975**, *31*, 1655−1658, and ref 6.

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Supporting Information Available: Full experimental details and characterization data for all new compounds described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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