Pergamon

Tetrahedron Letters, Vol. 38, No. 18, pp. 3257-3260, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00579-0

Low-Temperature Oxyanion-Accelerated Vinylcyclopropane-Cyclopentene Rearrangement. Reaction of 2-(2-(Trimethylsilyl)-ethenyl)cyclopropyl Acetates with Methyl Lithium

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Abstract: Reactions of four diastereomeric 2-(2-(trimethylsilyl)ethenyl)cyclopropyl acetates **7**, derived from enol silyl ether **4** and Fischer carbene complex **6**, with 2.2 equiv of MeLi at -80 ° to -30 °C afforded cyclopentenol **8** as a single diastereomer and acyclic enol silyl ethers **9** via the corresponding cyclopropanolates in ratios depending on the vinylsilane geometry. Predominant formation of **8** over **9** from (*Z*)-**7** irrespective of the stereochemistry at C-1 was observed. This is the first example of oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement which proceeds at unprecedentedly low temperatures. © 1997 Elsevier Science Ltd.

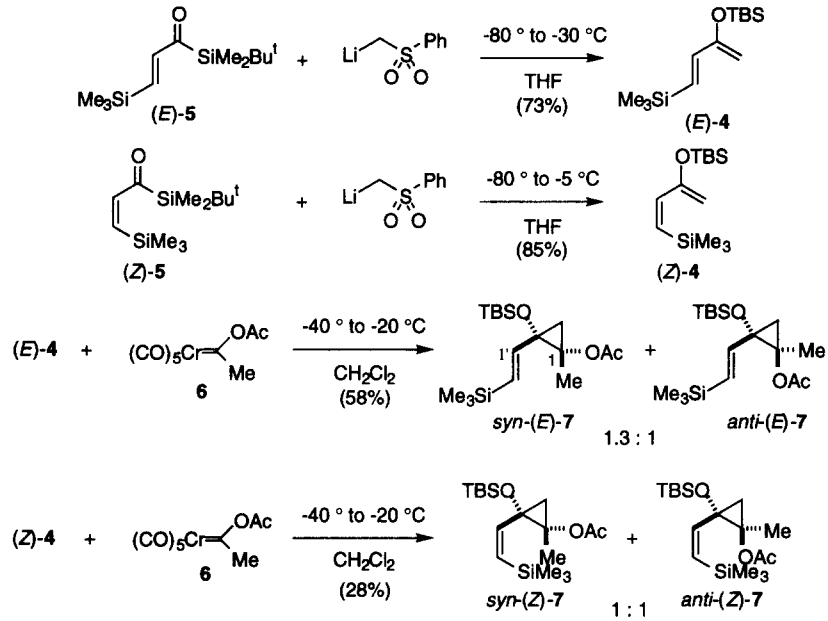
Although vinylcyclopropane-cyclopentene rearrangements have proven to be of considerable synthetic utility, the reaction suffers from a serious limitation in that the rearrangement only proceeds at high temperature, normally higher than 250 °C.[1] Danheiser found that an oxyanion substituent on the cyclopropane ring dramatically accelerated the rearrangement.[2] Even in these cases, however, the reaction requires temperatures in excess of 25 °C and the use of a highly dissociative medium such as HMPA. We now report the first example of an oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement[3] that proceeds at temperatures below -30 °C.

In connection with our investigation of the mechanism of the [3 + 2] annulation between β-heteroatom-substituted acryloylsilane and the lithium enolate of alkyl methyl ketone,[4] we became interested in whether the rearrangement of 2-(2-(trimethylsilyl)ethenyl)cyclopropanolate (**1**) to cyclopentenol (**2**) could proceed at low temperatures below -30 °C. To examine this possibility, we sought a synthetic route that would allow the rapid generation of the cyclopropanolate **1**, even at -80 °C. After considerable experimentation, we found that the reaction of 2 equiv of MeLi with the corresponding cyclopropyl acetate (**3**), prepared by the reaction of a dienol silyl ether (**4**) with an acetoxy carbene complex, was suitable for this purpose.

Thus, the dienol silyl ethers **4**, derived from (β-(trimethylsilyl)acryloyl)silanes (**5**)[5] and lithiomethyl phenyl sulfone according to Reich's protocol,[6] were treated with in situ generated acetoxy carbene complex

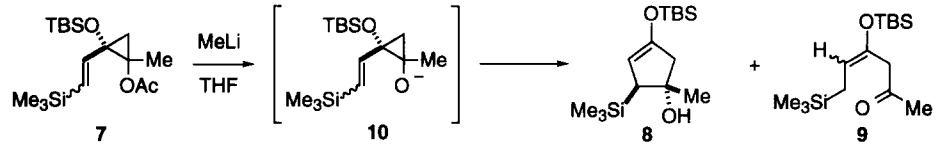
(**6**)[7,8] affording separable vinylcyclopropyl acetates **7** (Scheme 1). The stereochemical assignments of **7** were based on the presence of cross peaks between 1-Me and H-1' in NOESY experiments.

Scheme 1



Reactions of the cyclopropyl acetates **7** with MeLi (2.2 equiv) were performed in THF (0.02 M) at -80 °C for 30 min and at -80 °C followed by warming to -50 °C and -30 °C over 30 min, respectively, and quenching with a solution of acetic acid (1 equiv) in THF. In most cases, a single cyclopentenol (**8**)[9] and unsaturated ketone (**9**),[10] a ring opened product, were obtained (Table 1).[11,12] The product distribution depends upon the vinylsilane geometry, but is unaffected by the *syn/anti* stereochemistry between the *tert*-butyldimethylsiloxy (TBSO) and acetoxy groups. Particularly noteworthy is the substantial formation of **8** from (*Z*)-**7** even at -80 °C in contrast to the reaction with (*E*)-**7**, wherein **8** is not formed under these conditions.

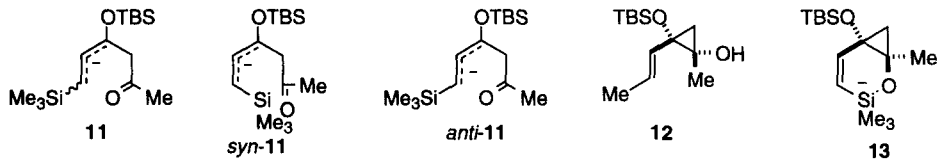
Table 1



7	conditions	yield (%)		7	conditions	yield (%)	
		8	**9**			**8**	**9**
syn-(*E*)	-80 °C, 30 min	0	81	*syn*-(Z)	-80 °C, 30 min	52	20
syn-(*E*)	-80 ° to -50 °C	45	40	*syn*-(Z)	-80 ° to -50 °C	61	5
syn-(*E*)	-80 ° to -30 °C	54	31	*syn*-(Z)	-80 ° to -30 °C	76	16
anti-(*E*)	-80 °C, 30 min	0	89	*anti*-(Z)	-80 °C, 30 min	59	10
anti-(*E*)	-80 ° to -50 °C	45	39	*anti*-(Z)	-80 ° to -50 °C	72	6
anti-(*E*)	-80 ° to -30 °C	63	34	*anti*-(Z)	-80 ° to -30 °C	76	14

The dependency of the product ratio upon the vinylsilane geometry seems to be inconsistent with a pathway entailing intramolecular attack of the freely-rotating delocalized allylic anion intermediate **11**, generated by ring opening followed by allylic delocalization of the resulting carbanion, on the carbonyl group. Also, a simple concerted [1,3]-sigmatropic shift is incompatible with the observation that the same cyclopentenol (**8**) is obtained irrespective of the vinylsilane geometry and of the stereochemistry at C-1 of **7**.

Although the precise mechanism to account for the results remains unclear, the trimethylsilyl group should play a crucial role in the rate acceleration because 2-propenylcyclopropanol derivative **12**[13] was recovered unchanged after exposure to methyl lithium (1 equiv) at -80 ° to -30 °C. A plausible mechanism involves kinetically controlled ring-closure of the silicon-stabilized allylic carbanion intermediates *syn*-**11** and *anti*-**11** which form from (*Z*)-**10** and (*E*)-**10**, respectively. Thus, the cyclization of *syn*-**11** to **8** can occur faster than that of *anti*-**11** and conformational interconversion between *syn*- and *anti*-**11** for some unknown reason. Another attractive but unverified mechanism is one where **8** is produced only via [1,3]-sigmatropic shift of the internally O-Si coordinated intermediate **13** which is directly derived from *anti*-(*Z*)-**7** and can be reversibly generated from three other diastereomeric cyclopropanolates **10** by ring-opening, geometric isomerization and ring-closure sequence. More facile rearrangement of **13** to **8** is presumably due to its fixed conformation suitable for the overlap of the orbitals required for the rearrangement, and the stereochemical course is in agreement with that predicted by orbital symmetry considerations, assuming the methyl group is bulkier than the solvated oxyanion.



In summary, we have demonstrated the first examples of oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement to proceed at unprecedentedly low temperatures. Further studies aimed at clarification of the reaction mechanism of the [3 + 2] annulation as well as of the vinylcyclopropane rearrangement are now underway in our laboratory and will be reported in due course.

Acknowledgment. Acknowledgment is made to the Research Foundation for Pharmaceutical Sciences and the Grant-in-Aid for Scientific Research (No. 08672416 (K. T.)) from the Ministry of Education, Science, Sports, and Culture, Japan for partial support of this research.

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9. The relative stereochemistry was assigned on the basis of NOESY experiments and of comparison with spectroscopic data of related compounds.[4]
10. The *E*/*Z* ratios were variable although the *E* isomer always predominated, and were independent of the ratios of **8** and **9**.
11. No *E*/*Z* and *syn*/*anti* isomerization was observed in a small amount of **7** recovered from the reaction mixture.
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(*Received in Japan* 3 *March* 1997; *revised* 17 *March* 1997; *accepted* 21 *March* 1997)