A New Synthetic Method for Cyclic Allenes and Acetylenes. Cleavage of a C-C Bond Directed by a Silyl Group

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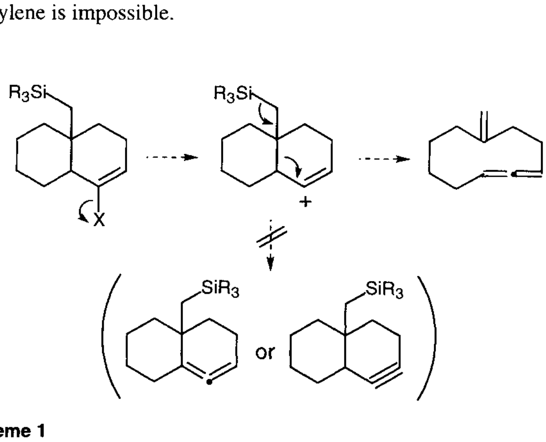
Dedicated to Professor E. J. Corey in recognition of his significant contributions to the art of organic synthesis

Abstract: A new synthetic method for medium-sized cyclic allenes and acetylenes was developed on the basis of a C-C bond cleavage directed by a silyl group. An enol triflate derived from 6-(silylmethyl)-10-siloxybicyclo[4.4.0]decan-2-one was heated at 150 °C in DMF to afford ten-membered allene in good yield. A cyclodecyne derivative was also prepared from the regioisomeric enol triflate.

Cleavage of a bridging C-C bond in bicyclic system[1] is one of the most practical route to medium-sized carbocycles. While anionic transformation such as Grob-type fragmentation reactions[2] are commonly employed for these purposes, it seems to be difficult to achieve the similar conversion under acidic conditions which involve side reactions such as β-elimination or rearrangement of a cationic intermediate.

In order to develop a new ring expansion reaction via selective cleavage of a C-C bond, we designed a δ-silyl vinyl cationic species[3] as shown in Scheme 1. We envisioned that the high lability of the vinyl cation[4] would favor the bond cleavage assisted by silyl group. Moreover, the vinyl cation would not undergo undesirable β-elimination reaction because the formation of a bicyclic allene or acetylene is impossible.

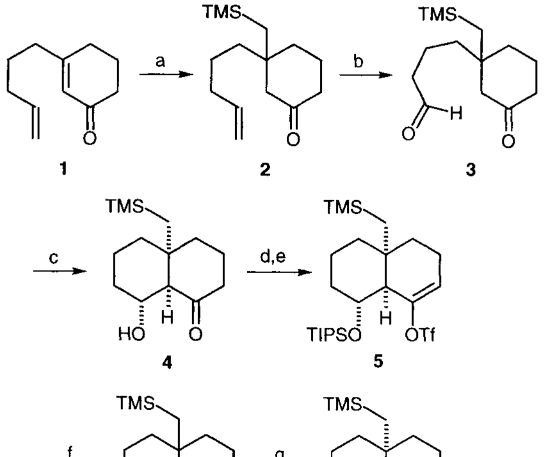


Scheme 1

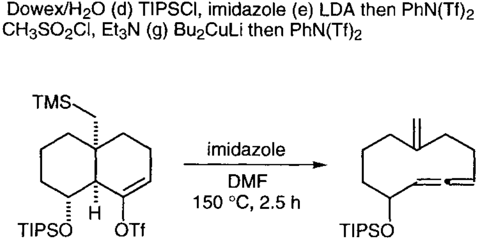
Two types of the fragmentation precursors were prepared as shown in Scheme 2. Introduction of the silylmethyl group was easily achieved by a 1,4-addition reaction using the corresponding Grignard reagent. The intramolecular aldol reaction of ketoaldehyde **3** under acidic conditions gave ketol **4** as a single diastereomer.[5] The hydroxy group of **4** was protected by a triisopropylsilyl group, and the ketone was converted into enol triflate[6] **5** through kinetically controlled generation of the lithium enolate. On the other hand, treatment of enone **6** with Bu_2CuLi followed by *N*-phenyltrifluoromethanesulfonimide afforded enol triflate **7** regioselectively.

Initial attempts to activating the enol triflates by treating with Lewis acids failed to give the fragmentation product. For example, reaction of enol triflate **5** with $EtAlCl_2$ merely resulted in substitution of the trifluorosulfonate with chloride.

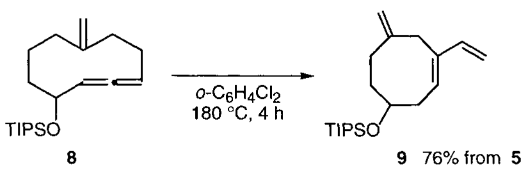
However, a thermal decomposition was found to induce the desired transformation. Thus, on heating in DMF at 150 °C for 2.5 h in the presence of imidazole, **5** afforded cyclic allene[7] **8** in good yield. Interestingly, prolonged reaction period gave a small amount of cyclooctene derivative **9** along with **8** via Cope rearrangement. The higher strain energy seems to make cyclic allene **8** much less stable than **9**,[8] and heating of the former in *o*-dichlorobenzene at 180 °C induced complete transformation to the latter.



Scheme 2. (a) $TMSCH_2MgCl$, CuI (b) O_3/MeOH then Me_2S (c) Dowex/H_2O (d) TIPSCl, imidazole (e) LDA then $PhN(Tf)_2$ (f) CH_3SO_2Cl, Et_3N (g) Bu_2CuLi then $PhN(Tf)_2$

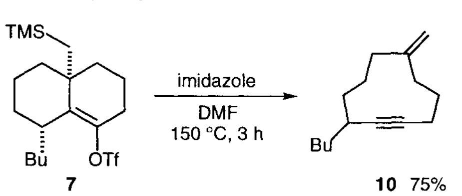


(1)



(2)

On the other hand, the reaction of enol triflate **7** gave cyclodecyne derivative **10** in good yield.



(3)

Enol triflate **5** remained unchanged in *o*-dichlorobenzene even after heating at 180 °C, which indicates that the polarity of the solvent is essential for the fragmentation reaction. Therefore, the dissociation of the enol triflate moiety into the vinyl cation is assumed as the rate-determining step. It has been reported that the generation of a 1-cyclopentenyl cation[9] from the corresponding enol triflate is quite difficult because of the *sp*-like character of a vinyl cationic carbon. Indeed, five-membered enol triflate **12** failed to give an eleven-membered allene, while allene **13** was obtained from bicyclo[5.4.0]-undecane derivative **11**.

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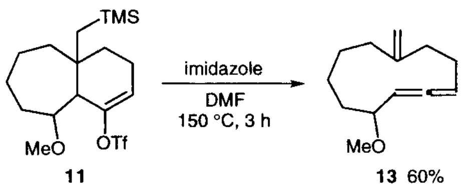
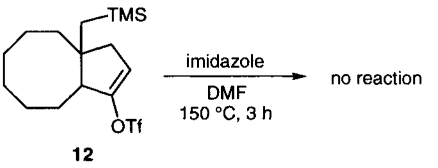


(4)



(5)

In conclusion, a new synthetic method for medium-sized cyclic allenes and acetylenes from bicyclic enol triflates was developed on the basis of the selective C-C bond cleavage reaction directed by silicon. It should be noted that the utilization of a vinyl cation in synthetic reactions has been limited because of its high lability. The present reaction may also show the potential of a vinyl cation in organic synthesis.

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References and Notes

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(5) The stereochemistry of ketol **4** was assigned as follows: The *cis* configuration of the angular methyne proton and the silylmethyl group was determined by observation of NOE. The stereochemistry of the hydroxy group was assigned by the coupling constant (J = 11 Hz) between the angular methyne proton and the α-proton of the hydroxy group.

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(8) PM3 calculations on 6-methylene-1,2-cyclodecadiene and 7-methylene-2-vinylcyclooctene were performed, and the results indicate that the latter is 11.1 kcal/mol more stable than the former.

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