nius CAD4 diffractometer using Mo K_{α} radiation to a maximum 2θ value of 50°. The structure was solved with use of the heavy-atom method (SHELXS 86) and blocked-matrix least-squares procedures (SHELX 76) on the CRAY-2S/4-128 supercomputer.
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Anionic Cyclizations of Alkyllithiums to Vinyl Sulfides

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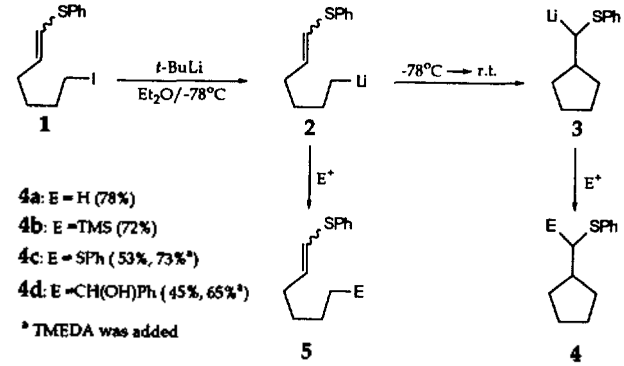
Ring-forming reaction is one of the most important operations in organic synthesis and generally involves cationic[1] and radical cyclizations.[2] Much less attention has been given to anionic cyclizations,[3] although a number of recently developed methods employ anionic cyclizations for the construction of 5-membered rings.[4] In anionic cyclizations, an internal electrophilic acceptor should be survived during the generation of a highly reactive carbanion. Alkynes and unactivated alkenes have been normally utilized as electrophilic acceptors. The major advantage of the anionic cyclization over the radical and cationic cyclization may be that it is possible to functionalize the initially formed cyclization product by the reaction with various electrophiles, whereas both trapping the radical intermediate before it abstracts hydrogen atom from tributyltin hydride and the formation of 5-membered ring *via* the cationic intermediate are normally difficult to achieve in a reliable manner.

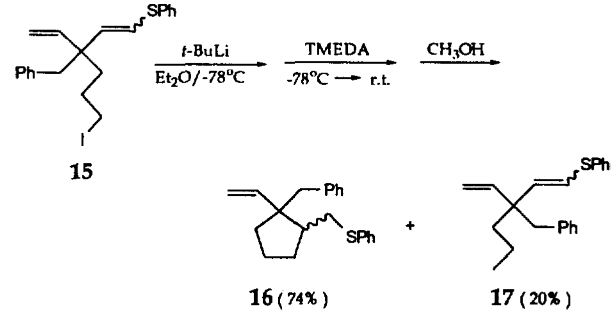
We have been interested in developing internal electrophiles which could promote anionic cyclizations under mild conditions as well as introduce useful functional groups for further transformations. Since it has been known that the vinyl sulfide showed a good electrophilicity toward organolithium reagents,[5] we have examined whether the vinyl sulfide might be served as the internal electrophile in anionic cyclization reactions.

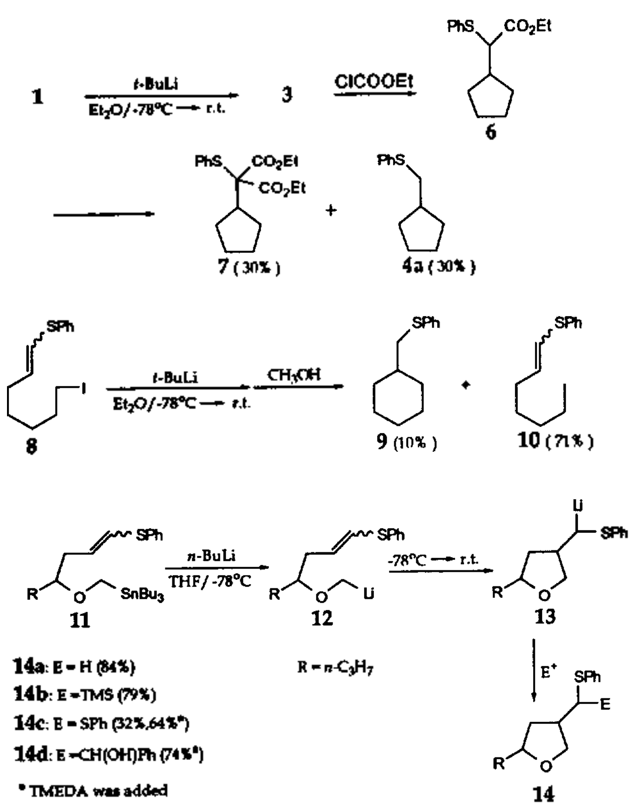
The anionic cyclization was studied with 6-iodohex-1-enylphenyl sulfide (**1**). **1** was prepared from 6-bromohexanal by routine four-step operations.[6] Reaction of **1** with *t*-butyllithium (2.2 equiv) in deoxygenated diethyl ether at −78℃ would generate **2** which underwent anionic cyclization upon warming to room temperature to afford **4** in 78% yield without the formation of **5** after quenching **3** with methanol. Apparently, the metal-halogen exchange proceeds much faster than proton abstraction from the vinyl sulfide group to afford α-lithiovinylphenyl sulfide anion.[7] It is noteworthy that the cyclization did not occur when the reaction was carried out at −78℃, even though a vinyl sulfide is expected to be a much better electrophilic acceptor than an unactivated alkene. The initially formed cyclization product could be quenched with several electrophiles such as chlorotrimethylsilane and diphenyl disulfide as shown in Scheme I. The isolated yields of the quenched products were relatively low when diphenyl disulfide, benzaldehyde, and ethyl chloroformate were employed as electrophiles. The yields were considerably improved by the addition of TMEDA (2 equiv) to the reaction mixture.[8] In the case of using ethyl chloroformate as an electrophile, *bis*-ethoxycarbonylated compound **7** was isolated in 30% yield along with 30% of **4a** due to the abstraction of the relatively acidic hydrogen in **6** by **3**. The anionic cyclization of 7-iodohept-1-enylphenyl sulfide (**8**) was not successful under the similar conditions, yielding **9** in 10% yield along with the direct quenched product in 71% yield.



Scheme 1.

Since the formation of tetrahydrofurans is synthetically useful due to the possible applicability toward natural product synthesis, we briefly studied anionic cyclizations of α-alkoxylithium using a vinyl sulfide as the electrophilic acceptor.[9] To study the anionic cyclization of α-alkoxylithium, we prepared **11** from 2(2-bromo)-ethyl-1,3-dioxolane by a seven-step sequence.[10] Reaction of **11** with *n*-butyllithium in tetrahydrofuran at −78℃ should give **12** which underwent cyclization upon warming the reaction mixture to room tem-





Scheme 2.

perature to afford **13**. **13** was further reacted with several electrophiles to afford **14** as shown in Scheme II. The addition of TMEDA was beneficial to improve the isolated yields of cyclized products. The stereochemistry of the substituents has not been determined, although 1,3-*cis* isomer was reported to be normally a major product.[9c]

Finally, a vinyl sulfide *vs*. an unactivated alkene competition as an internal electrophile has been studied. Treatment of **15** with *t*-butyllithium (2.2 equiv) in diethyl ether at -78 ℃ for 0.5 h followed by the addition of TMEDA (2.0 equiv) at -78℃ and warming to room temperature afforded the cyclized product **16** (74%) along with the direct protonated product **17** (20%) after trapping with methanol. When the reaction was carried out in tetrahydrofuran under the similar conditions, a mixture of **16** (53%) and **17** (40%) was isolated.

The results obtained in this study clearly demonstrate that a vinyl sulfide group is a much better electrophilic acceptor than an unactivated alkene and allows us to functionalize the cyclized products by the reaction with various electrophiles.

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10. (i) Mg, n-C_3H_7CHO, THF (53%). (ii) Ac_2O, pyridine (88%). (iii) PhSH, BF_3-Et_2O, CH_2Cl_2 (88%). (iv) MCPBA, CH_2Cl_2 (77%). (v) $(MeO)_3P$, DME (80%). (vi) NaOH, aq MeOH (92%). (vii) KH, Bu_3SnCH_2I, THF (47%).

The Complete ^1H NMR Study of Bicyclo[3.1.1]heptane Derivative for its Conformation

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In all the aspects of high-resolution NMR study, resonance assignment is one of the key that unlocks all of the information present in the spectrum. Therefore, the importance of correct assignment can never be overstated. For simple spectra with only a few widely dispersed resonances, assignment is more often than not a trivial exercise, but for narrow chemical shift ranges and extended spin systems, it can be a very severe problem and make even the structure determi-