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Efficient Preparation of Vinylcyclopropane by S_N' Cyclization of the Organolithium Derived from (E)-5-Iodo-1-methoxy-2-pentene

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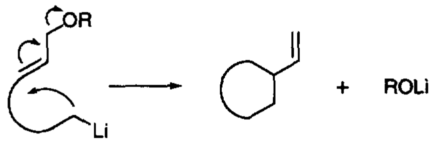
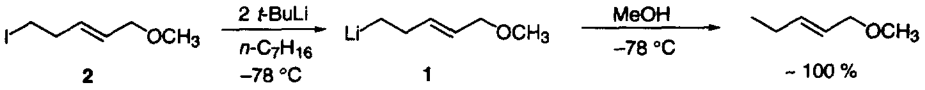
Abstract: (5-Methoxy-E-3-pentenyl)lithium (1), which may be prepared in virtually quantitative yield from the corresponding iodide by low-temperature lithium–iodine exchange, cyclizes with expulsion of the allylic methoxy on warming in the presence of TMEDA to afford vinylcyclopropane in 88 % yield. © 1997 Elsevier Science Ltd.

The intramolecular addition of an organolithium to a tethered olefinic bond bearing a leaving group at the distal allylic position offers a conceptually simple route to vinyl-substituted ring structures. A number of groups have exploited such intramolecular S_N'cyclizations[1] for the preparation of a variety of medium-size rings, such as vinylcyclopentanes,[2,3] vinylcyclohexanes,[2] (3-vinyl)tetrahydrofurans,[4] etc.[5] Although much less information is available concerning utility of this approach for the synthesis of strained rings,[1] it is of some interest to note that the initial report of an S_N' cyclization initiated by an unstabilized organometallic involved formation of a three-membered ring by intramolecular 3-exo addition of a Grignard reagent to a tethered allylic ether.[6]

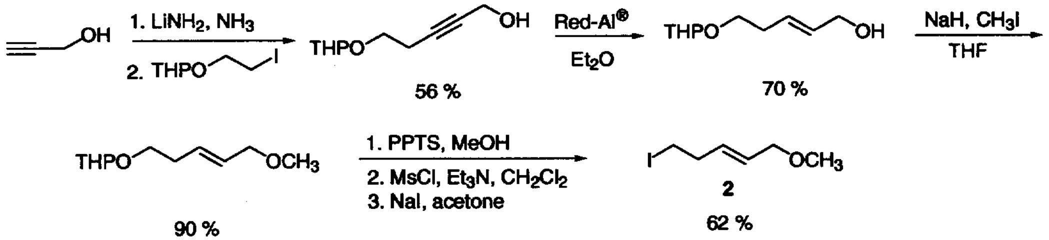


In light of our interest in the cyclization of unsaturated organolithiums,[7] we were prompted to investigate the facility of a prototypical 3-exo-S_N' ring-closure for the preparation of vinylcyclopropane. As detailed below, intramolecular S_N' displacement of lithium methoxide from (5-methoxy-E-3-pentenyl)lithium (**1**) affords vinylcyclopropane in excellent yield. Organolithium **1**, in turn, may be generated from readily available (E)-5-iodo-1-methoxy-2-pentene (**2**) by low temperature lithium–iodine exchange.

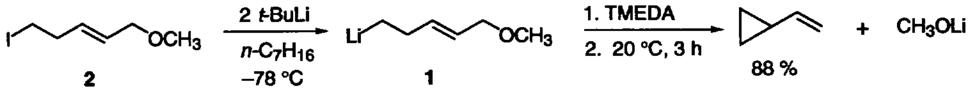
The requisite iodide precursor (**2**) was prepared from propargyl alcohol and THP-protected 2-iodoethanol[8] in straightforward fashion as illustrated in Scheme 1.[9] Conversion of **2** to (5-methoxy-E-3-pentenyl)lithium (**1**) required modification of our general protocol for lithium–iodine exchange[10] so as to minimize the quantity of volatile solvents used in the preparation. Thus, treatment of an approximately 0.5 M solution of **2** in dry *n*-heptane with 2.0 molar equiv of commercially available *t*-BuLi in *n*-heptane at –78 °C for 30 min under argon cleanly generates **1** as demonstrated by the fact that quench of such reaction mixtures with oxygen-free MeOH delivered (E)-1-methoxy-2-pentene in essentially quantitative yield. It should be noted that the lithium–iodine exchange with *t*-BuLi is generally not successful when conducted in pure hydrocarbon solvents;[10] the ease with which **2** may be prepared in heptane is most likely due to the presence of an ether oxygen in the substrate.[11]



Scheme 1



Cyclization of **1** was effected, as shown below, by addition of 2.0 equiv of dry, oxygen-free TMEDA to a –78 °C solution of **1** in heptane and allowing the resulting mixture to warm and stand at ~20 °C for 3 h. The reaction mixture was then washed with water and dried ($MgSO_4$). GC analysis revealed that the intramolecular S_N'reaction had proceeded in >93 % yield; vinylcyclopropane[12] was readily isolated in 88 % yield by preparative GC (10-ft, 20 % SE-30 on Anakrom U at 60 °C). Although a number of other routes to vinylcyclopropane have been reported,[13] the S_N'-approach is unique in giving a high yield of pure product free of isomeric impurities.



Acknowledgment. This work was supported by the Connecticut Department of Economic Development.

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9. Satisfactory C/H analyses have been determined for all previously unreported compounds and their ^1H NMR and ^{13}C NMR spectra are fully in accord with the assigned structures. Spectroscopic data for iodide **2**: ^1H NMR ($CDCl_3$) δ 2.57–2.62 (m, 2H), 3.14 (t, J = 7.18 Hz, 2H), 3.30 (s, 3H), 3.84–3.85 (m, 2H), 5.57–5.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 4.71, 36.22, 57.86, 76.62, 128.96, 131.94. Anal Calcd for $C_6H_{11}OI$: C, 31.88; H, 4.90. Found: C, 31.56; H, 4.50.
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11. It might be noted that treatment of allyl methyl ether with an alkyllithium in ethereal solvents leads to abstraction of an allylic proton to give (1-methoxy)allyllithium, see: Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560.
12. Vinylcyclopropane: ^1H NMR ($CDCl_3$) δ 0.36 (dt, J = 6.28 Hz, J = 4.47 Hz, 2 H), 0.69 (ddd, J = 8.15 Hz, J = 6.28 Hz, J = 4.47 Hz, 2H), 1.35 – 1.43 (m, 1 H), 4.82 (ddd, J = 10.00 Hz, J = 1.78 Hz, J = 0.32 Hz, 1 H), 5.04 (ddd, J = 17.05 Hz, J = 1.78 Hz, J = 0.50 Hz, 1H), 5.32 (ddd, J = 17.05 Hz, J = 10.00 Hz, J = 8.71 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 6.65, 14.69, 111.48, 142.49. These ^{13}C chemical shifts are virtually identical to those previously reported for vinylcyclopropane [Rudolph, A.; Weedon, A. *Can. J. Chem.* **1990**, *68*, 1590]; *viz.*, δ 6.67, 14.76, 111.50, 142.61
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