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Radical Cyclization of β-Allenic Oxime Ethers

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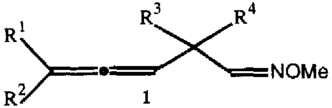
Abstract: β-allenic O-methyl oximes undergo a free radical hydrostannylation reaction to afford cyclopentenes bearing a protected amine group and a vinyl stannyl fonction. These compounds were destannylated to yield the corresponding cyclopentenes.

We have recently reported on the Lewis acid mediated cyclization of allenic compounds bearing nucleophilic groups at γ or δ position. These reactions provide six[1] or seven [2] membered rings. From related works, it occured to us that an easy access to five membered rings would be possible by using the free radical cyclization route[3].

It was expected that the selective addition of a radical species, and specially tributyltin radical to the allene moiety could generate a new radical center. This, in turn, could react with a suitable acceptor group within the molecule to give cyclopentene derivatives. In this regard, several radical acceptors can be considered[4].

We now describe the results obtained with β-allenic O-methyloximes **1**.



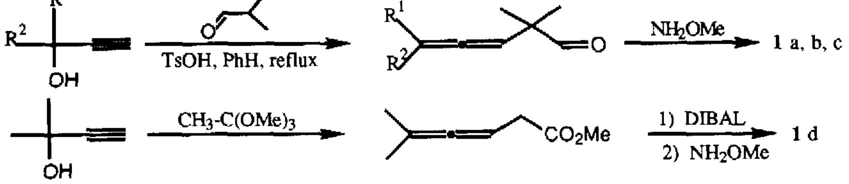
1

a) $R^1, R^2, R^3, R^4 = CH_3$ b) $R^1, R^3, R^4 = CH_3$; $R^2 = H$

c) $R^1, R^3, R^4 = CH_3$; $R^2 = C_2H_5$ d) $R^1, R^2 = CH_3$; $R^3, R^4 = H$

These substrates have been prepared in two or three steps starting from the corresponding acetylenic alcohols according to scheme 1.

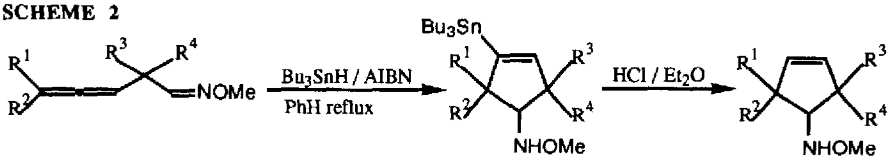
SCHEME 1



Refluxing a 0.02 M benzene solution of the allenic oxime ether **1** containing tributyltin hydride and AIBN leads to the cyclized compound **2** with good yields[5,8]. The tributyltin radical adds selectively on the central allenic carbon atom. The allylic radical so formed adds to the carbon of the oxime function in an intramolecular way. For the **1b** and **1c** derivatives, the cyclization affords a mixture of two isomers (**2b**: 65/35; **2c**: 89/11)[6] The major one is, in both case, that where the methyl group on C-5 and the amino function are cis.

To remove the tributyltin group, several well known methods have been tried (AcOH, SiO_2, BuLi). Finally, we succeeded by using hydrochloric acid in diethylether[7,8]. In this way, we obtained cyclopentenes **3** bearing a N-methoxy amine function (scheme2).

SCHEME 2



1, 2, 3

	2	3
a	77%	82%
b	74	77
c	91	83
d	37	53

The overall reaction sequence gives fairly good yields (63 to 75%) except for **3d**. In every case, the vinyltin intermediate **2** have been isolated and therefore could be used for various transformations[9].

References and Notes

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5. In a typical experiment, Bu_3SnH (1.2 eq.) and AIBN (O.2eq.) are added to a 0.02 M benzene solution of the O-methyl oxime **1**. After degassing this solution with a stream of argon, it is refluxed until the disappearance of the starting material. The reaction is monitored by TLC. After evaporation of the solvent, the crude product is purified by flash chromatography over silica gel.
6. The isomeric ratios were determined by ^1H NMR spectrum integration.
7. In a typical experiment, the stannyl derivative **2** is treated with a saturated solution of HCl in diethylether at room temperature. After evaporation of the solvent, the residue is taken up in ether and washed off twice with an aqueous solution of $NaHCO_3$ and once with water. The organic layer is dried ($MgSO_4$) and evaporated to afford the crude cyclopentene **3** which is flashchromatographed over silica gel.
8. All new compounds have spectral data (IR, ^1H NMR, ^{13}C NMR) and combustion analysis in good agreement with the structures assigned. For example: compound **2a**: ^{1}HNMR ($CDCl_3$, TMS, 400 MHz) δ 0.87 (t, 7Hz, 15H), 0.9 (s, 3H), 0.94 (s, 3H), 1,132 (s, 3H), 1,139 (s, 3H), 1.29 (sext., 7.4Hz, 6H), 1,45 (m, 6H), 3.01 (s, 1H), 3.49 (s, 3H), 5.42 (t, 19.1Hz, 1H); ^{13}CNMR ($CDCl_3$, TMS, 400MHz) δ 151.04 (C), 149.25 (CH), 76.12 (CH), 60.79 (CH_3), 52.74 (C), 48.69 (C), 31.15 (CH_3), 30.23 (CH_3), 29.24 (CH_2), 27.44 (CH_2), 23.81 (CH_3), 23.09 (CH_3), 13.75 (CH_3), 9.94 (CH_2). Compound **3a**: ^{1}HNMR ($CDCl_3$, TMS, 400MHz) δ 0.94 (s, 6H), 1.13 (s, 6H), 3.03 (s, 1H), 3.48 (s, 3H), 5.31 (s, 2H); ^{13}CNMR ($CDCl_3$, TMS, 400MHz) δ 137.74 (CH), 75.55 (CH), 60.79 (CH_3), 47.20 (C), 30.05 (CH_3), 23.18 (CH_3). Analysis Calcd. for $C_{10}H_{19}NO$ C=70.96, H=11.31, N=8.27; Found C=70.98, H=11.19, N=8.18.
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