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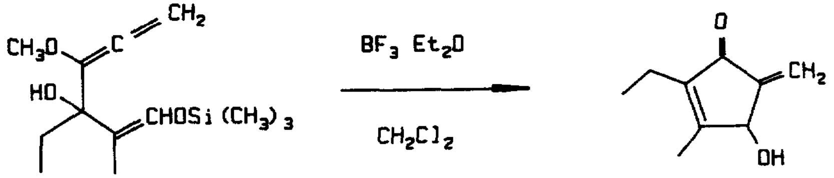
ALLENE ETHERS FOR THE CATIONIC CYCLOPENTANNELATION

Marcus A. Tius*[1], J-B. Ousset, Donald P. Astrab, Abdul H. Fauq and Sanjay Trehan

Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822, U.S.A.

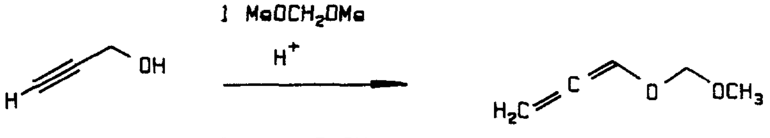
Summary: Only allene ethers having a group which is capable of departing as a stable cation participate successfully in the cationic cyclopentannelation reaction.

It was recently brought to our attention that an abstract of our work on the cationic cyclopentannelation of allene derivatives[2] had appeared in Fieser and Fieser's "Reagents for Organic Synthesis", Volume 12.[3] The abstract contains a subtle, but very significant error, and it is the purpose of this Letter to correct this error and to communicate some of our unpublished work in this area.



1 2 (1)

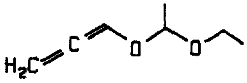
The abstract states that treatment of **methoxy**allene derivative **1** with boron trifluoride etherate in methylene chloride produces methylene cyclopentenone 2 (eq 1).[3] In fact, this reaction produces **none** of the cyclic material **2**! Most of our work has been done with the (methoxy)methoxyallene **3**. The preparation of this material has been accomplished in two steps from propargyl alcohol (eq 2).[4] In order to avoid the methoxymethylation step, we subjected commercially available methyl propargyl ether to the potassium tert-butoxide catalyzed isomerization reaction and we isolated methoxyallene. To our surprise the adducts of trimethylsilyl ethers of hydroxymethylene ketones with the anion derived from this allene (cf. **1**) failed to undergo the desired cyclization reaction. We subsequently prepared allene ethers **4**, **5**, **6** and **7** using the method of eq 2. Each of these allenes was converted to the corresponding lithio anion **8** which was added to trimethylsilyl vinylogous ester **9** to produce adducts **10** (Scheme 1). Treatment of the adducts **10** derived from allenes **4**, **5**



propargyl alcohol

3 (2)

and **6** with boron trifluoride etherate led in each case to methylene cyclopentenone **11**. The adduct from allene **7** (**10**, R=n-propyl) and the adduct from methoxyallene (**10**, R=methyl) failed to undergo detectable cyclization to **11**.



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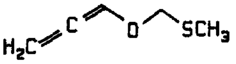

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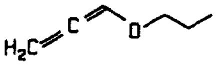

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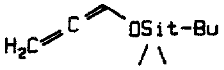

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These observations are most easily explained by postulating that the acid catalyzed cyclopentannelation reaction proceeds through a resonance stabilized intermediate **12**, and that the rapid loss of R as a stable cation is a requirement for the efficient cyclization. Although allene ethers 3, **4**, **5** and **6** have all been used succesfully, the first reagent which was used in this reaction, (methoxy)methoxyallene 3, should be considered the reagent of choice. The ease of preparation of 3 and its stability to storage recommends its use in the cationic cyclopentannelation reaction.

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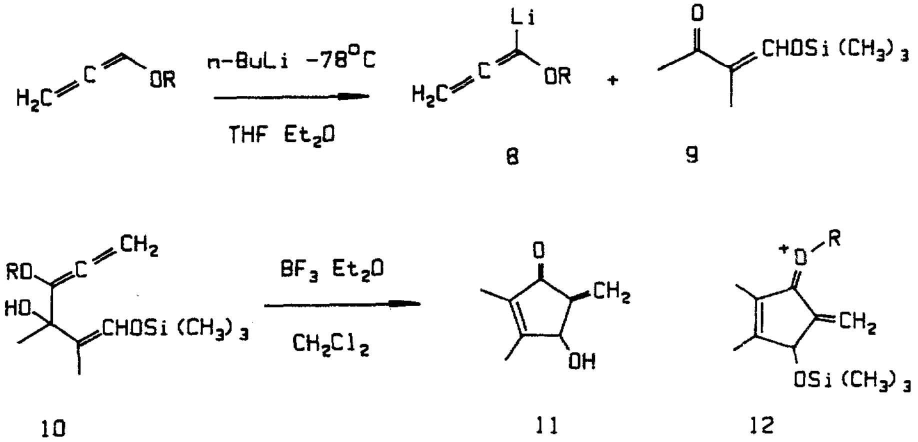
Scheme 1



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