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DIRECT SUBSTITUTION OF SECONDARY ALLYLIC ALCOHOLS WITH O-SILYLATED KETENE ACETALS IN 3.0 M LITHIUM PERCHLORATE-DIETHYL ETHER - AN ALTERNATIVE TO THE [1,3] SIGMATROPIC REARRANGEMENT OF ALLYL VINYL ETHERS

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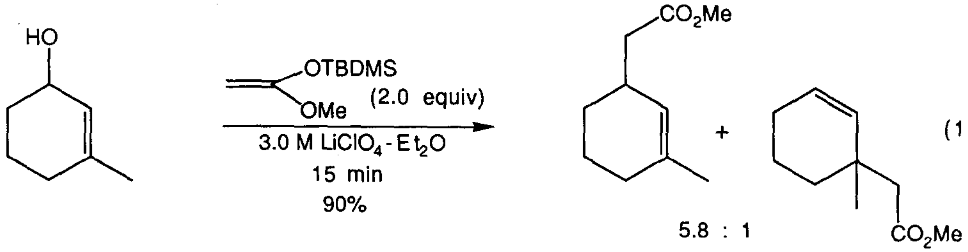
Abstract: Allylic alcohols of type **1** undergo unprecedented substitution with O-silylated ketene acetals in 3.0 M lithium perchlorate-diethyl ether.

As a result of our continuing interest in the use of lithium perchlorate in diethyl ether to promote organic reactions,[2,3] we wish to report that allylic alcohols of the type depicted in Equation 1 undergo extremely facile substitution in 3.0 M lithium perchlorate-diethyl ether upon addition of the silyl ketene acetal derived from methyl acetate.[4] This unprecedented carbon-carbon bond forming reaction represents a useful alternative to the facile [1,3] sigmatropic rearrangement of allyl vinyl ethers reported previously (Equation 2).[3]



(1)

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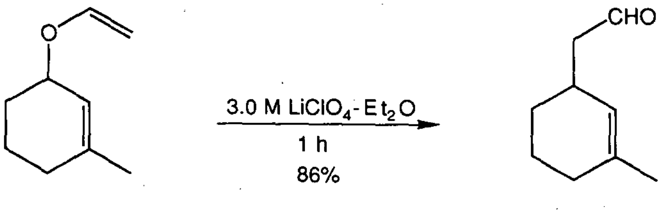
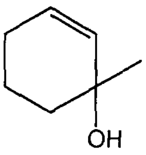


(2)

During the course of our investigation on the lithium perchlorate-diethyl ether promoted [1,3] rearrangement of allyl vinyl ethers,[3] we observed that 1-methylcyclohex-2-en-1-ol (**4**) upon brief exposure (10 min) to 3.0 M lithium perchlorate-diethyl ether rearranged to the corresponding secondary allylic alcohol (cf **1**). Interestingly exposure of a 0.2 M solution of **1** in 3.0 M lithium perchlorate-diethyl ether to 2.0 equiv of the *tert*-butyldimethylsilyl ketene acetal derived from methyl acetate afforded in excellent yield (90%) a mixture of **2** and **3** in a ratio of 5.8:1. Similar results were obtained with **4**. The concentration of the lithium perchlorate in diethyl ether (LPDE) appears to be important. For example use of 2.0 M LPDE in the reaction illustrated in Equation 1 results (93%) in formation of silyl ether **5** along with **2** and **3** in a ratio of 2:6.4:1 respectively. Upon going to 1.0 M LPDE the reaction rate is slowed considerably and the amount of **5** produced is substantially increased (ratio of **2**:**3**:**5** is 5.5:1:4.0).



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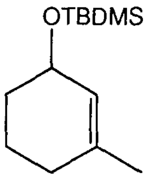

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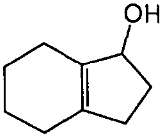
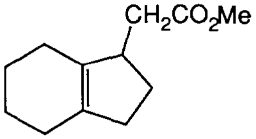
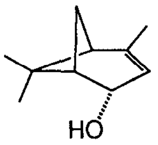
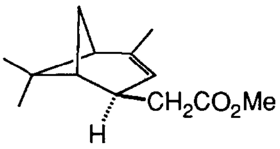
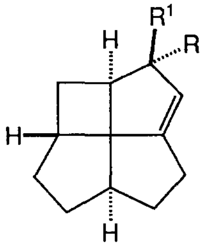
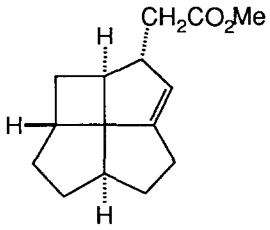
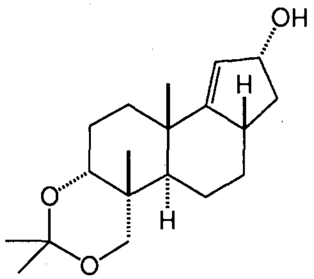
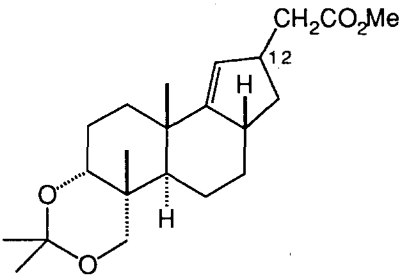
This novel carbon-carbon bond forming reaction can be applied to a number of substrates as illustrated in Table 1. In all cases, reaction is complete within 15 min. Attempts to carry out this substitution reaction on cyclohexenol and geraniol only led to formation of the corresponding *t*-butyldimethylsilyl ethers in excellent yields. It thus would appear that a requirement for carbon-carbon bond formation is that the allylic alcohol be secondary and possess γ,γ-disubstitution.

All of the reactions in the Table including the transformations of **1** into **2** and **3** require 2.0 equiv of silyl ketene acetal. Interestingly, use of 1.0 equiv of silyl ketene acetal gives rise to only a 50% yield of product. In order to gain insight into the mechanism of this unique reaction, substrate **1** was labelled with ^{18}O and the reaction was conducted in 3.0 M LPDE using 2.0 equiv of silyl ketene acetal. No ^{18}O was found in either **2** or **3**. Brief exposure (10 min) of the lithium alkoxide of **1** (0.2 M in 3.0 M LPDE) to 1.0 equiv of silyl ketene acetal in the presence of 1.0 equiv of *tert*-butyldimethylsilyl triflate gave rise to an excellent yield of **2** and **3**, in a ratio of 6.6:1. In the absence of the added *tert*-butyldimethylsilyl triflate the reaction proceeds at a snails pace. Note that there is no reaction if the *tert*-butyldimethylsilyl ether **5** is treated with

Table I. Substitution of Allylic Alcohols with 1-Methoxy-1-(t-butyldimethyl siloxy)ethylene in 3.0 M Lithium Perchlorate-Diethyl Ether[a]

entry	substrate	product(s)	% yield[b]
1			86
2			93[c]
			
3	R=H, R^1=OH		74
4	R=OH, R^1=H		79
5			95[d]

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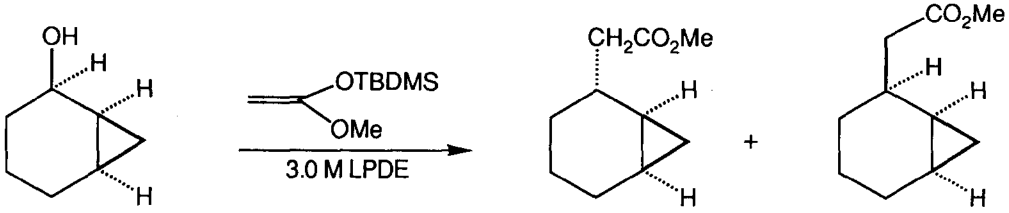
[a] All reactions were conducted at ambient temperature employing a 0.2 M solution of allyl alcohol in 3.0 M lithium perchlorate-diethyl ether containing 2.0 equiv of 1-methoxy-1-(*t*-butyldimethylsiloxy)ethylene and were complete in 15 min. [b] Isolated yields. [c] Approximately 5% of the rearranged allylic transposed isomer was isolated. [d] A 1:1 mixture of epimers at C(12) was obtained.

2.0 equiv of silyl ketene acetal in 3.0 M LPDE. Additional studies are underway to determine the mechanism of this reaction.

In principle the chemistry depicted in Equation 1 should be applicable to cyclopropyl carbinols. Indeed cyclopropyl carbinol **6** upon exposure (15 min) to 2.0 equiv of 1-methoxy-1-(*t*-butyldimethylsiloxy)ethylene in 3.0 M LPDE undergoes smooth transformation into a 4:1 mixture of **7** and **8** in 75% yield. Further studies are underway to determine the scope of this novel reaction.



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References

1. J. Stewart and Dagmar K. Riley Graduate Fellow, 1991-1992.
2. Grieco, P.A.; Nunes, J.J.; Gaul, M.D. *J. Am. Chem. Soc.*, **1990**, *112*, 4595. Grieco, P.A.; Cooke, R.J.; Henry, K.J.; Vander Roest, J.M. *Tetrahedron Lett.*, **1991**, *32*, 4665. Henry, K.J.; Grieco, P.A.; Jagoe, C.T. *ibid*, **1992**, *33*, 1817. Also see Grieco, P.A. *Aldrichimica Acta*, **1991**, *24*, 59.
3. Grieco, P.A.; Clark, J.D.; Jagoe, C.T. *J. Am. Chem. Soc.*, **1991**, *113*, 5488.
4. Similar results have been observed by Professor William H. Pearson. We are grateful to Professor Pearson for informing us of his work prior to publication.

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