α-Functionalized Conjugated bisallenes: Attractive substrates for transition metal catalysis

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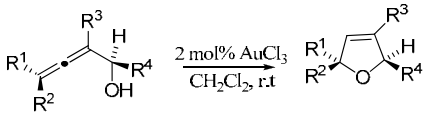
Introduction

Although the chemistry of (unfunctionalized) conjugated bisallenes is very rich, there are only few reports on functionalized derivatives,[1] and no systematic study on the synthesis and transformation of functionalized conjugated bisallenes has been reported to date. This is quite intriguing since the development of new methods for the synthesis of functionalized conjugated bisallene derivatives can provide precursors for highly complex carbo- and heterocycles, employing efficient and atom-economical routes.

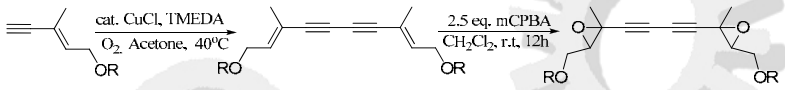
By taking advantage of the high reactivity and axial chirality of allenes[2], our group has established an efficient and stereoselective synthesis of 2,5-dihydro-furans by gold-catalyzed cycloisomerization of α-hydroxyallenes[3].



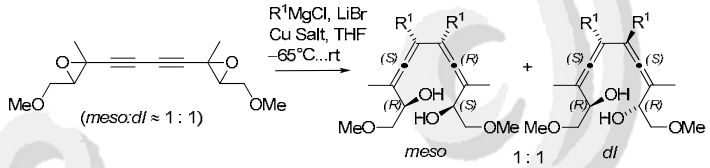
Herein, we disclose a novel, convenient and stereoselective approach to conjugated bis(α-hydroxyallenes), as well as their cyclization to bis(2,5-dihydrofuran) derivatives and 2-allenyl-substituted 2,5-dihydrofurans.

Results

Synthesis of Bis(propargyloxiranes)



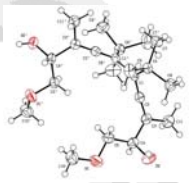
Copper-mediated S_N2'-Substitution[4] of Bis(propargyloxiranes) Conjugated Bisallenol Synthesis

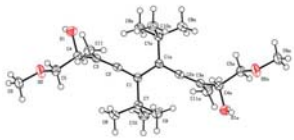


R¹ = *i*-Pr: 68% (CuBr · SMe_2) / 85% (CuCN)
R¹ = *t*-Bu: 74% (CuBr · SMe_2) / 82% (CuCN)

Table 1: Generality of Bisallene Synthesis

Entry	R	R^1	Yield(%)
1	Methyl	Ethyl	12
2	Methyl	Phenyl	33
3	Benzyl	*i*-Propyl	55
4	Benzyl	*t*-Butyl	54
5	TBS	*i*-Propyl	57
6	TBS	*t*-Butyl	58
7	TBS	Benzyl	21
8	TBS	Ethyl	28





Copper-mediated S_N2'-Substitution of Bis(propargyloxiranes) at very low temperatures: Synthesis of Propargyloxirane substituted α-allenol

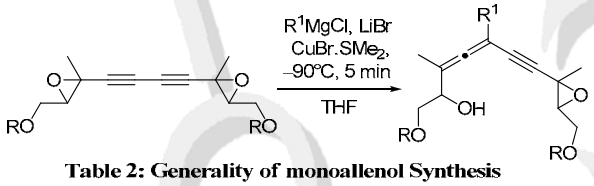
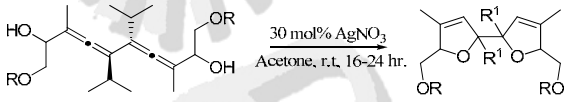


Table 2: Generality of monoallenol Synthesis

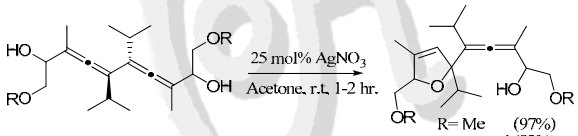
Entry	R	R^1	Yield(%)
1	Methyl	*i*-Propyl	49
2	Methyl	*t*-Butyl	53
3	Benzyl	*i*-Propyl	49
4	TBS	*i*-Propyl	54
5	TBS	*t*-Butyl	59
6	TBS	*n*-Butyl	57

$AgNO_3$-catalyzed[5] Cycloisomerization of Bisallenols: Synthesis of bis(2,5-Dihydrofurans)



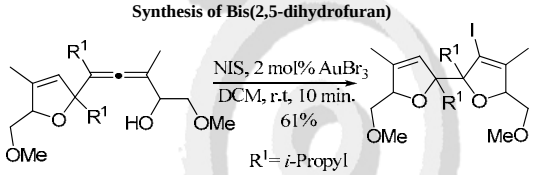
R= Me R¹= Et (59%)
R= TBS R¹= Et (53%)
R= TBS R¹= Bn (62%)

$AgNO_3$-catalyzed[5] Cycloisomerization of Bisallenols: Synthesis of 2-Allenyl-substituted 2,5-Dihydrofurans



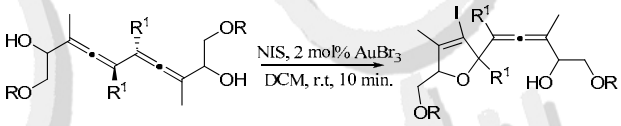
R= Me (97%)
R= Benzyl (83%)
R= TBS (90%)

NIS-mediated[6] Gold-catalyzed Cycloisomerization: Synthesis of Bis(2,5-dihydrofuran)



R¹= *i*-Propyl

NIS-mediated Gold-catalyzed Cycloisomerization: Synthesis of 2-Allenyl-3-iodo-2,5-dihydrofurans



Entry	R	R^1	Product	Yield(%)
1	Methyl	*t*-Butyl	**7a**	81
2	TBS	*t*-Butyl	**7g**	80
3	Benzyl	*t*-Butyl	**7e**	69
4	Methyl	*i*-Propyl	**7b**	60

Conclusion:

We have developed a convenient method for the synthesis of highly substituted conjugated bis(α–allenols)[7] and propargyloxirane substituted mono(α–allenols) and thereby providing a successful route to novel bis(2,5-dihydrofurans) and 2-allenyl-2,5-dihydrofuran derivatives. Further studies regarding the synthesis and application of conjugated bis(α–allenols) and their cycloisomerization products are currently under investigation.

References

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