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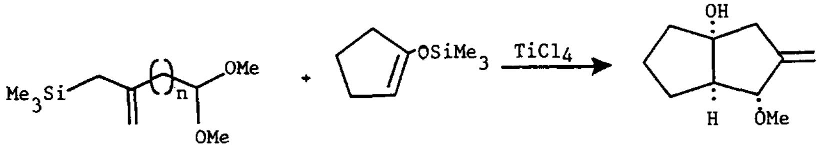
BIFUNCTIONAL ANNULATING REAGENTS: THE USE OF NOVEL ALLYLSILANES FOR THE ONE-POT PREPARATION OF SIX AND SEVEN-MEMBERED RINGS

Thomas V. Lee*, Raymond J. Boucher and Caroline J.M. Rockell
(School of Chemistry, The University, Bristol BS8 1TS, England).

Summary: Preliminary details of a new strategy for the synthesis of five, six, and seven-membered rings by use of novel allylsilane reagents are described.

The preceding communication described some interesting chemistry for a series of acetalstannanes which, although of value in forming five-membered rings, are of limited or no use in the synthesis of cyclohexanes or cycloheptanes.[1] We have therefore made a detailed study of a series of complementary reagents, the allylsilanes (1) to (3), having already disclosed the utility of (1) in forming cyclopentanes by reaction with an O-silylated enolate in the presence of a Lewis acid.[2] This paper describes the reactions of (2) and (3) to form cyclohexane and cycloheptane derivatives, so providing us with a general strategy for the one-pot preparation of five, six and seven-membered rings.



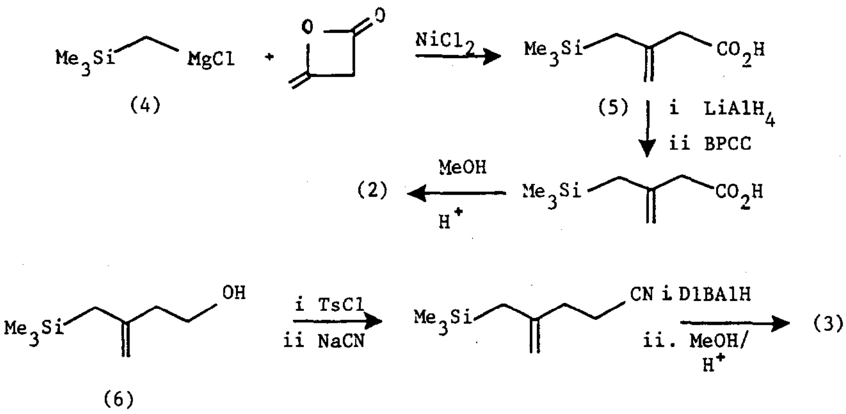
(1) n = 0

(2) n = 1

(3) n = 2

The preparations of (2) and (3) are shown in SCHEME 1. The known reaction of the Grignard reagent (4) with diketene in the presence of anhydrous nickel (11) chloride gave the allylsilane (5)[3] which was reduced, oxidised[4] and protected to provide an overall 36% yield of the required bifunctional annulating reagent (2). The corresponding allylsilane (3) was obtained from the alcohol (6) which was an intermediate in the above route. Tosylation and cyanide displacement gave a nitrile which was readily converted to (3) in 46% overall yield.

SCHEME 1



The results of the reaction of these allylsilanes with O-silylated enolates is shown in the TABLE. We know that initial reaction with trimethylsilyl trifluoromethanesulphonate forms predominantly the 1 isomer (7)^5, which is not usually isolated unless required, but is treated with titanium tetrachloride to form the cyclized product (8) as a mixture of cis and trans isomers.^{6,7} From a synthetic viewpoint this is not a disadvantage since we can make good use of one of the features of these allylsilanes over our previously described organotin bifunctional reagents^8, viz. the provision of additional functionality for manipulation in the newly formed ring. Thus ketone formation and elimination of water gives an enone (9) in yields of 62-67% which are of greater flexibility in synthesis than the alcohol precursors.

In summary, bifunctional annulating reagents such as (1) - (3) are the basis of a novel general one pot annulation procedure, currently applicable to the preparation of five, six and seven-membered rings. The ability of the two reactive centres in these reagents to be activated under one set of conditions, but sequentially, is an important feature, not least since it negates the need for the laborious preparation of cyclization precursors.^{9} Additionally unlike the only other one-pot bifunctional annulating reagents to have been reported^{10} these are not limited to the synthesis of one ring size.

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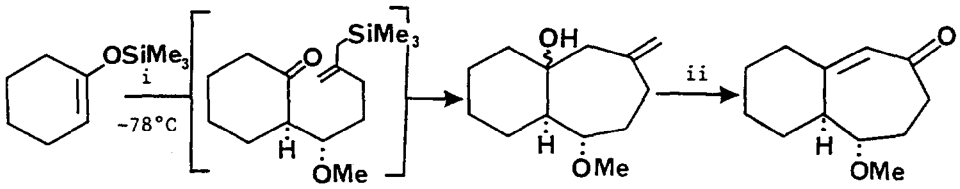
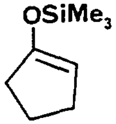
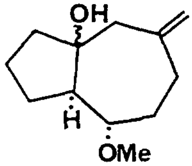
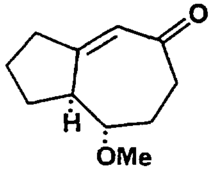
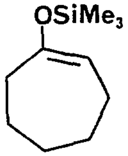
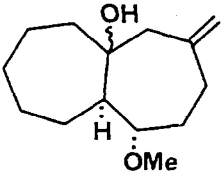
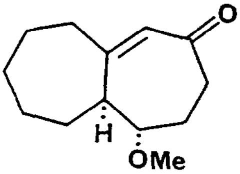
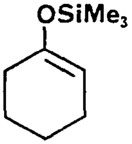
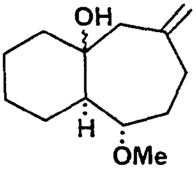
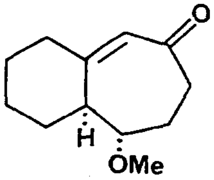
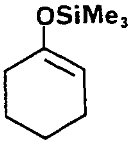
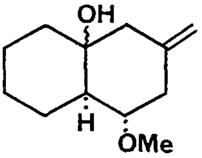
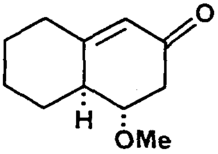
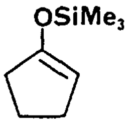
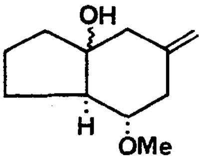
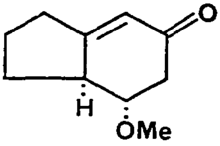
TABLE

(3) +



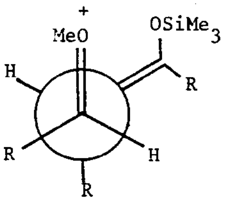
(7) (8) (9)

REAGENT	ENOL	(8)	(9)
(3)			
(3)			
(3)			
(2)			
(2)			

i = TMSOTf-TiCl$_4$; ii = OsO$_4$-NaIO$_4$/SOCl$_2$

REFERENCES AND NOTES

1. Preceding communication.
2. T.V. Lee, K.A. Richardson and D.A. Taylor, *Tetrahedron Letters,* 1986, 27, 5021.
3. K. Itoh, T Yogo and Y. Ishii, *Chem. Letts.,* 1977, 103.
4. The use of bispyridinium chlorochromate is essential in this oxidation, since unlike other oxidants it minimises the production of an α,β-unsaturated aldehyde in which the methylene group has moved into conjugation.
5. D. Seebach and V. Prelog, *Angew. Chem., Int. Ed. Engl.,* 1982, 21, 654.
   This stereochemical outcome can be explained by considering a transition state in which the two reactants approach one another with the topology shown below. (D. Seebach and J. Golinski, *Helv. Chim. Acta.* 1981, 64, 1413).



6. The actual ratio of isomers and the factors controlling their formation are currently under study and will be published in due course.
7. All new compounds gave satisfactory analytical and/or spectral data.
8. T.V. Lee and K.A. Richardson, *Tetrahedron Letters,* 1985, 26, 3629.
9. cf G. Majetich, J. Defauw, K. Hull and T. Shawe, *Tetrahedron Letters,* 1985, 26, 4711, and references therein.
10. B.M. Trost, *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 1.
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