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NOVEL ANNULATION REACTIONS: A SIMPLE PREPARATION OF SPIROCYCLES AND AN ALLYLSILANE BASED BIFUNCTIONAL ACCEPTOR-DONOR ANNULATING REAGENT

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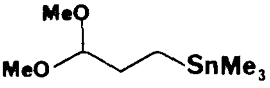
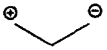
Summary: *A simple, one pot, stereoconvergent synthesis of spirocycles has been achieved in excellent yield. Further studies on one step bifunctional annulating reagents have resulted in the development of a new allylsilane based cyclopentannulation reaction.*

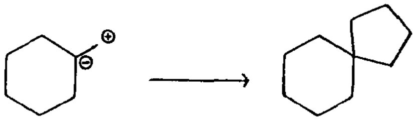
We recently described the first one pot bifunctional annulating reagent (1) which in its reaction as an acceptor-donor species, represented by the formalism (2), provided a direct preparation of five-membered rings.[1] A useful extension to this chemistry would involve the reaction of (1) with a synthon, such as (3), which is an expression of the pattern of reactivity in the O-silylated enolate of a cyclic carboxaldehyde. As shown in SCHEME 1, the reaction of the acetalstannane (1) with such enolates, in the presence of trimethylsilyltrifluoromethanesulphonate (TMSOTf), gave the aldehyde (4) which cyclizes, after treatment with titanium tetrachloride, to the alcohol (5). In order to overcome some difficulties associated with the handling of the alcohol (5) it was immediately oxidised to the ketone (6) in 83% yield from the enolate.



(1)



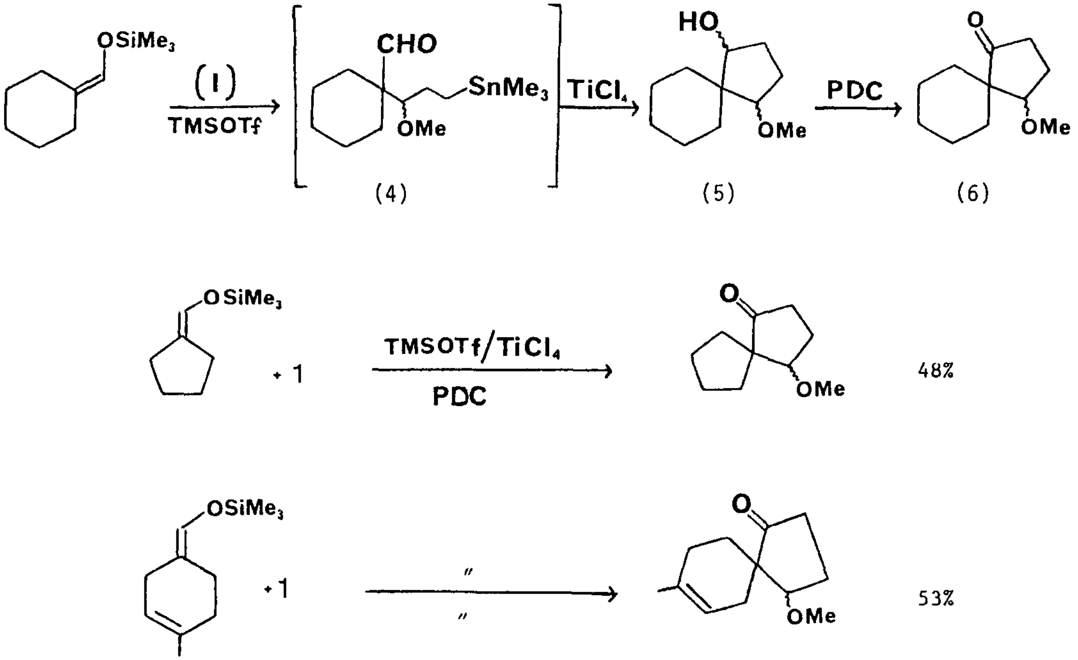
(2)



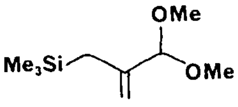
(3)

Besides being a highly efficient and simple way of constructing spirocyclic carbon skeletons the new method has the additional advantage that the products contain two oxygen functions, at different oxidation levels, in equivalent positions. The two functions are thus distinguishable and interconvertible so making the reaction stereoconvergent at the newly formed quaternary centre. The new method should therefore be of great utility in the synthesis of spirocyclic natural products which we are in the process of demonstrating.

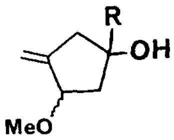
SCHEME 1



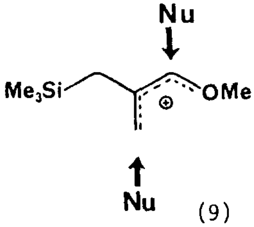
Further consideration of the formalism (2) suggests that the allylsilane (7) will react in the same manner as (1) with O-silylated enolates but to give a product (8) possessing additional and useful funtionality. However, one potential limitation of such a reagent[4] is



(7)



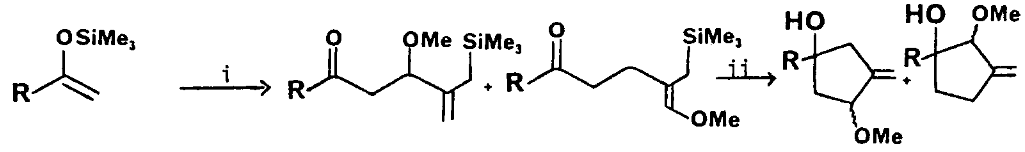
(8)

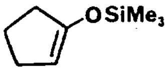
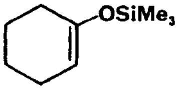
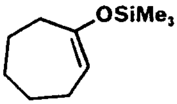
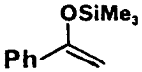


(9)

that upon reaction with a Lewis acid, an unsymmetrical allyl cation (9) may be formed possessing two sites for nucleophilic attack. SCHEME 2 shows the site of attack to be dependent upon the structure of the enol ether with the enol ethers (10) and (11) being the only ones to date to display synthetically useful selectivity.[5]

SCHEME 2



	Direct : Allylic	Overall % Yield
 (10)	1 : 9	48
 (11)	1 : 3.2	60
	1 : 1.27	57
	1 : 1.63	47

i, TMSOTf, -78°C; ii, $TiC\ell_4$, -78°C

One way of achieving greater selectivity may be by variations in the silyl group or the acetal groups of (7), and such studies are currently being undertaken.

Acknowledgements. *We would like to thank the SERC for support of this work.*

REFERENCES AND NOTES

1. T.V. Lee and K.A. Richardson, *Tetrahedron Letters*, 1985, 26, 3629.

2. We have shown by n.m.r. that formation of (4) does occur but have not yet determined the stereochemistry of the reaction at the acetal carbon.

3. Used immediately after preparation (Me_3SiCl, DMF, Et_3N) from the corresponding aldehyde (J. Liska and G. Greull, *Org. Synth. Coll. Vol. V*, p.320).

4. Prepared by acetalisation of the aldehyde derived from Swern oxidation of a known alcohol (B.M. Trost, D.M. Chan and T.N. Nanninga, *Org. Synth.*, 1984, 62, 58).

5. High field n.m.r. studies confirm that, as expected, the stereochemistry about the new ring junction, is exclusively *cis*.

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