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A SILICON DIRECTED DIENE SYNTHESIS

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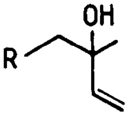
Summary: A convenient method for the conversion of a series of aldehydes into substituted dienes is reported which uses silicon as a control element.

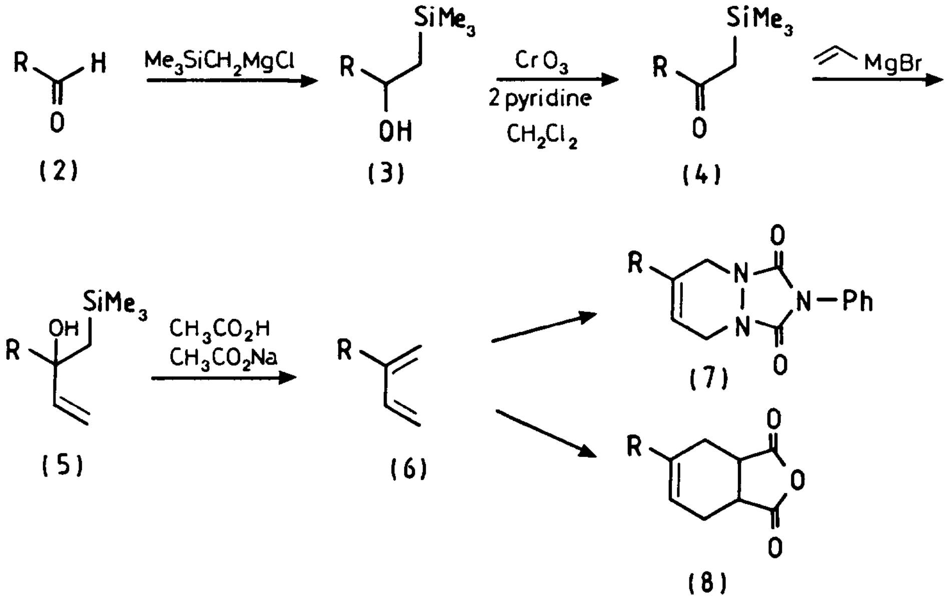
As part of a synthetic approach to the taxane group of natural products[1] we required a reliable way of converting an aldehyde into a 2-substituted diene. The very poor regioselectivity observed in the acid catalysed dehydration of structures such as (1) led us to the idea that the insertion of a strategic $SiMe_3$ group into the structure



(1)

would stabilise the cationic intermediate probably involved in the elimination, and lead to selective loss of $SiMe_3$ in preference to a proton.[2] Although a Peterson elimination has been used in a synthesis of 1-trimethylsilylbutadiene[3] and other dienes,[4] to the best of our knowledge no case had been reported where a $SiMe_3$ group causes double bond formation to take place in one arm of a branching carbon framework leading to a single diene. We now report results which show that the method is a convenient and reliable method for transforming an aldehyde into a range of substituted dienes.

Dihydrocinnamaldehyde (2a) reacted with Me_3SiCH_2MgCl to give the silyl alcohol (3a) as an oil in 91% yield. Careful Collins oxidation using a reaction time of 1 minute led to the silyl ketone (4a) in 97% yield.[5] The preparation of α-silyl ketones such as (4a) by reaction of Me_3SiCH_2MgCl with an ester has been reported,[6] however, it was less successful than the above procedure in our hands. Addition of vinyl magnesium bromide to the ketone (4a) produced the tertiary allylic alcohol (5a) in 78% yield which underwent Peterson elimination on treatment with acetic acid and sodium acetate leading to the diene (5a) in 73% yield.[7] The ^1H n.m.r. spectrum of (6a) ($CDCl_3$, 400 MHz) showed δ2.50 (2H, broad t J 9 Hz, H-4), 2.80 (2H, broad t J 9 Hz, H-5), 4.99 (1H, broad s, H-1'), 5.03 (1H, broad s, H-1'), 5.07 (1H, d J 11 Hz, H-1), 5.27 (1H, d J 18 Hz, H-1), 6.40 (1H, d x d J 11 and 18 Hz, H-2), 7.10-7.35 (5H, m, aromatic) other spectroscopic data was completely consistent with this structure. Clearly, exclusive loss of $SiMe_3$ has occurred leading to a single diene. The diene (6a) was converted into a crystalline Diels-Alder adduct in 72% yield with 4-phenyl-1,2,4-triazoline-3,5-dione.[8] A series of aldehydes have been subjected to this procedure as summarised in the Scheme 1 and Table.



Scheme 1

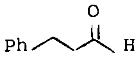
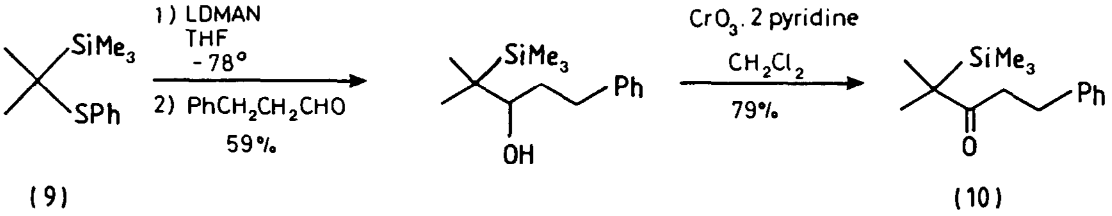
Aldehyde (2) RCHO	%Yield(3)	%Yield(4)	%Yield(5)	%Yield(6)	%Yield(7) or (8)
a 	91^a	97	78^a	73^a	72 $(7)^a$
b $C_6H_{13}CHO$	90	95	94	70	77 $(7)^a$
c 	90^a	86	88	50^a	-
d Ph-CHO	97	94^a	95	65	70 $(8)^a$
e $C_6H_{11}CHO$	85^a	93	84	60	76 $(7)^a$
f $C_9H_{19}CHO$	88	98	74	84^a	-

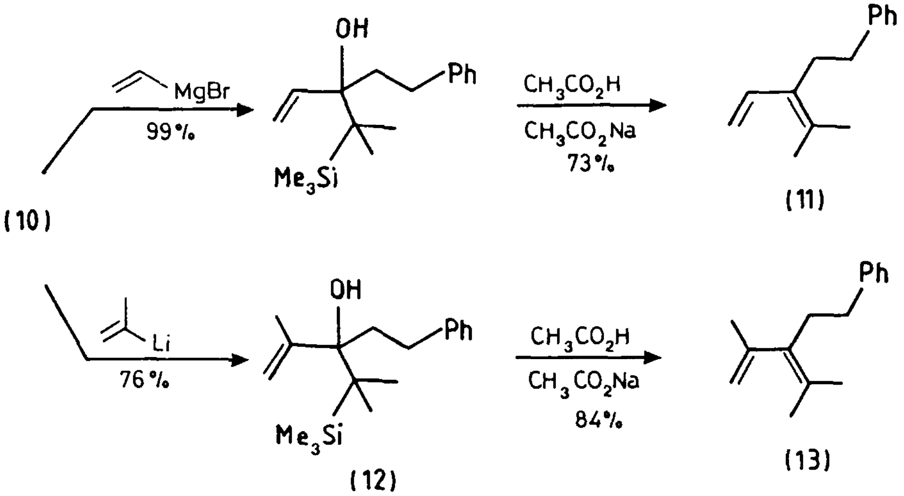
Table: All new compounds gave satisfactory ^1H, ^{13}C n.m.r., i.r., and mass spectral data; compounds giving correct microanalysis results are indicated (a) in the Table.

The route is readily extended to more highly substituted dienes using Cohen's procedure[9] for the generation of 2-lithio-2-trimethylsilylpropane from (9) as indicated in Scheme 2.



Scheme 2 LDMAN = Lithium 1-(dimethylamino)naphthalenide

Although vinyl magnesium bromide reacts readily with ketone (10) 2-propenyl magnesium bromide did not react, however, successful reaction was achieved using propenyl lithium generated by the Shapiro reaction on acetone trisyl hydrazone[10] to give (12) which gave the tetra-substituted diene (13) after elimination.



Scheme 3

The results indicate that the method described is a convenient route to 2-substituted dienes and that it is readily extended to the synthesis of more highly substituted dienes (11) and (13) which are difficult to prepare by other methods.

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References

1. P.A. Brown, P.R. Jenkins, J. Fawcett and D.R. Russell, J. Chem. Soc., Chem. Commun., 1984, 253.

2. These two points about the $-SiMe_3$ group are part of a useful series of generalisation about organosilicon chemistry in I. Fleming, 'Organic Silicon Chemistry', in 'Comprehensive Organic Chemistry', eds. D.H.R. Barton and W.D. Ollis, Vol. 3, p. 539, Pergamon, Oxford (1979).

3. M.J. Carter and I. Fleming, J. Chem. Soc., Chem. Commun., 1976, 679; M.J. Carter, I. Fleming, and A. Percival, J. Chem. Soc., Perkin I, 1981, 2415.

4. P.W.K. Lau and T.H. Chan, Tetrahedron Lett., 1978, 2383.

5. R. Ratcliffe and R. Rodehorst, J. Org. Chem., 1970, **35**, 4000; F. Hudrlik and D. Peterson, Tetrahedron Lett., 1974, 1133.

6. I. Fleming and A. Pearce, J. Chem. Soc., Perkin I, 1981, 251.

7. P.F. Hudrlik and D. Peterson, Tetrahedron Lett., 1972, 1785.

8. R.C. Cookson, S.S. Gupte, I.D.R. Stevens and C.T. Watts, Org. Syn., 1971, **51**, 121.

9. T. Cohen, J.P. Sherbine, J.R. Matz, R.R. Hutchins, B.M. McHenry, Paul R. Willey, J. Am. Chem. Soc., 1984, **106**, 3245.

10. A.R. Chamberlin and F.T. Bond, Synthesis, 1979, 44.

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