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THE CERIUM (III) MEDIATED REACTION OF TRIMETHYLSILYLMETHYL MAGNESIUM CHLORIDE WITH ESTERS AND LACTONES: THE EFFICIENT SYNTHESIS OF SOME FUNCTIONALISED ALLYLSILANES OF USE IN ANNULATION REACTIONS

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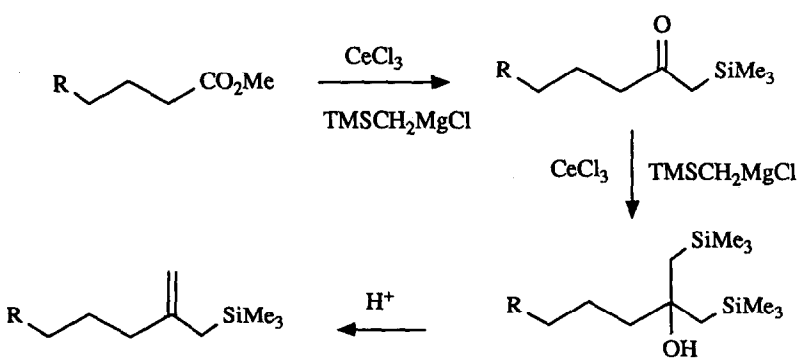
Summary: The use of cerium (111) chloride alters the chemoselectivity of the reaction of trimethylsilylmethyl magnesium chloride with ester-acetals and also greatly improves the efficiency of reaction with lactones. In addition it gives improved preparations of the useful intermediates (7), (13), (18),(20) and (22) and gives direct access to the valuable functionalised allylsilanes (1) to (3) of use in annulation reactions.

Introduction

Allylsilanes are of increasing importance in organic synthesis due to their undergoing, under mild conditions, highly regio- and stereocontrolled C-C bond formation[1]. They have been widely used for the allylation of most classes of electrophiles, notably in conjugate additions (the Sakurai reaction[2]) and in controlling polyene cyclizations[3].

One method for obtaining 2-substituted allylsilanes involves the reaction of esters with α-silyl substituted Grignard reagents. However yields in this reaction are typically low due to enolization of the intermediate α-silylketone competing with the addition of a second equivalent of the Grignard reagent. It was therefore significant when Narayanan and Bunnelle[4] recently reported that this problem can be overcome for simple



esters by premixing the α-silyl Grignard reagent with anhydrous cerium (III) chloride. The yields of the reaction are greatly increased presumably due to the enolization process now being appreciably slower as

nitrogen for 19h. The dark brown mixture was cooled, diluted with diethyl ether (30ml) and filtered through a bed of dry flash silica gel. Evaporation of the filtrate in vacuo gave the same aldehyde as above aldehyde (0.10g, 100%) which was used without further purification.

Dry methanol (22ml), trimethylorthoformate (44ml) and collidinium p-toluene sulphonate (0.01g) were added to crude aldehyde from either of the above reactions and the pale yellow solution was heated at reflux under nitrogen for 12h. The reaction was cooled to room temperature, evaporated in vacuo to a low volume and diluted with diethyl ether (50ml). The organic phase was washed with saturated sodium hydrogencarbonate solution (10ml), brine (10ml) and dried ($MgSo_4$). Evaporation afforded the crude acetal (31) as a pale yellow oil (0.93g). Purification by dry flash chromatography, eluting with petrol/ether (4:1) gave the acetal (3) as a colourless liquid (56%) R_F 0.6. Found: C, 61.07; H, 11.31. $C_{11}H_{24}O_2Si$ requires C, 61.05; H, 11.18%; ν_{max} 1640 (C = C), 1255, 1135 (C - O), 860 cm^{-1}; δ_H $CDCl_3$, 4.58 (1H, s, vinyl H), 4.51 (1H, s, vinyl H), 4.36 (1H, t, J=5.7Hz, $CH(OMe)_2$), 3.30 (6H, s, $(OMe)_2$) 1.98 (2H, m, CH_2), 1.73 (2H, m, CH_2), 1.51 (2H, s, CH_2SiMe_3), 0.015 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 146.78 (s), 106.95 (t) 104.08 (d), 52.59 (q), 32.92 (t), 30.62 (t), 28.87 (t), -1.39 (q); m/z, 216 (2%, M^+), 201, 185, 184, 169, 128, 111, 97, 88, 81, 80, 73.

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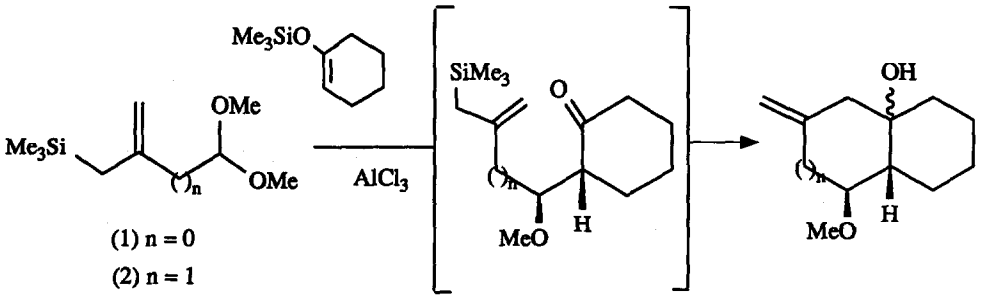
shown for other readily enolisable systems[5].This observation was of great interest to us since we have recently reported on the use of a range of allylsilane-acetals (**1**)-(**3**), which by chemoselective reaction of the acetal with an O-silylated enolate, as opposed to the allylsilane, permit the synthesis of five[6], six, and seven-membered fused[7] and spirocyclic rings[8]in one step.



(1) n = 0
(2) n = 1
(3) n = 2

The preparation of these compounds was the limiting factor in the development of these novel annulations since the routes to them involved multi step sequences which in places utilised highly capricious reactions. We have now extended the above observations on the value of using cerium (III) chloride in allylsilane preparation to esters that contain additional functionalities, including acetals. This has given us direct access to (**1**) to (**3**) and to a range of other useful allylsilanes, as we have reported[9]. This present paper describes this method in full plus its extension to further types of functionalised esters which establishes it as the most direct route to a wide range of functionalised 2-substituted allylsilanes.

Results and Discussion

General:- The conversion of functionalised esters to functionalised allylsilanes can be extended to a range of useful groups, each of which is discussed in detail below. However it must be emphasised that in every case the key to successfully forming allylsilanes by this method lies in a stringent requirement for using anhydrous conditions. We have found that obtaining anhydrous conditions in these reactions can be more difficult than in conventional Grignard reactions and is problematic due to the highly hygroscopic nature of cerium (111) chloride. Commercially available "anhydrous" cerium (111) chloride is of no use in these reactions, the rigorous dehydration and drying of the heptahydrate salt being the most reliable source of anhydrous cerium (111) chloride.

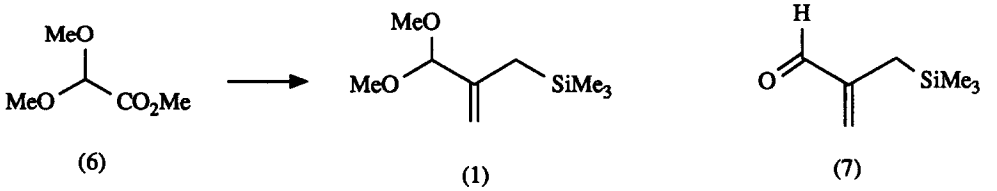
The nature of the reaction, or of any intermediates in the reaction, are not known with the heterogeneous conditions employed hindering structural studies. It seems unlikely to us that the formation of alkylcerium species is occuring since the reactions conditions employed, whereby the Grignard reagent and cerium salt are premixed for one hour at -78°C, are far removed from the normally much more rigorous conditions required in metal exchange processes. However the reaction does not proceed at all if any of the alternative orders of mixing are used. It may be that the cerium is involved in a direct interaction with the intermediate ketone species which enhances nucleophilic attack at the carbonyl and limits competitive enolization. A study of the use of soluble lanthanide salts in this reaction, so enabling easier structural studies, will clearly help to elucidate the mechanism of this reaction.

Acetal-esters:- One of the advantages of using this chemistry to prepare the above annulating reagents is that acetal-esters are now readily available by selective work-up of the ozonolysis products derived from

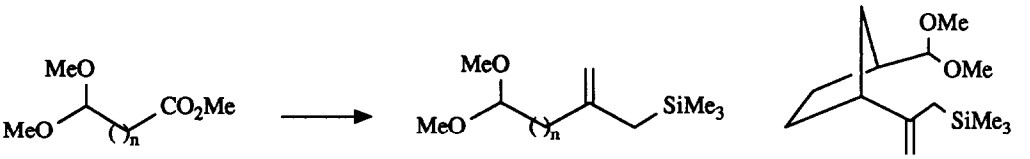
cycloalkenes[10]. The reaction of these bifunctional compounds in this cerium (111) chloride mediated Grignard reaction displays some interesting changes in chemoselectivity when compared with the conventional reaction. Thus addition of trimethylsilylmethylmagnesium chloride to the acetal ester (**4**) results in formation of the ester (**5**) as the only product containing a new carbon-carbon bond, formed by addition of the Grignard reagent at the acetal centre followed by elimination of methanol. In contrast to this premixing of the Grignard reagent with cerium (111) chloride causes a total change in chemoselectivity with nucleophilic attack now occurring at the ester function only, resulting after a second nucleophilic attack, in the formation of a tertiary alcohol. Upon mild acid treatment of this crude material, with silica gel, Peterson type elimination occurs to form the required allylsilane in good yield.

(4) + Me_3SiCH_2MgCl (5)

Alternatively in this process one has the option of producing allylsilane-aldehydes from these acetals by



(6) (1) (7)



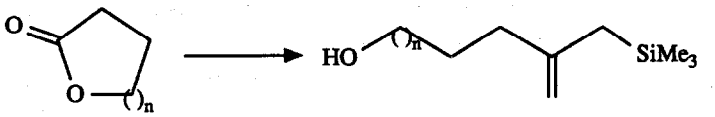
n = 1 = 48 %
n = 3 = 42 %
n = 4 = 78 %

(8)

53 % 95 %

prolonged acid treatment during the Peterson elimination step. For instance the ester (**6**) can be converted to either the acetal (**1**) in 45 % yield, of direct use in the annulation studies we are undertaking, or to the aldehyde (**7**) in 41 % which has previously been highlighted by Trost[11] as a valuable synthetic intermediate. A range of other acetal-esters have been successfully converted to allylsilanes such as (**8**), derived from norbornene. Additionally cyclic acetals and thioacetals also work well so emphasising the generality of this procedure.

Lactones:- Simple lactones are amongst the best substrates in this reaction, forming in good yields the

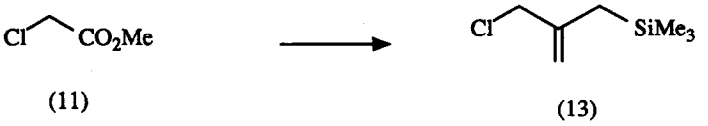


(9) n = 1 ; 74 %

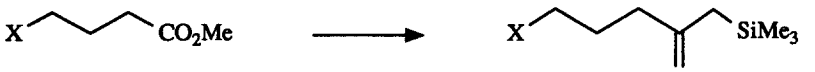
(10) n = 2 ; 62 %

hydroxyallylsilanes (**9**) and (**10**). The alcohol (**9**) is most useful being easily converted to the corresponding aldehyde by Swern oxidation and then to the annulating reagent (**3**) described above.

Halo-esters:- It is important with haloesters to use when possible chloro derivatives due to the complications that we have observed with bromo and iodo compounds. Thus the chloroesters (**11**) and (**12**) react very readily to give the corresponding chloroallylsilanes (**13**) and (**14**) in 55 % and 76 %. The former of these is the basis of a [3 + 2] annulating sequence developed by Knapp[12] but the development of a very much improved route to this compound enhances this process considerably since the allylsilane was previously prepared in 3 lengthy steps and 25 % yield. In contrast the bromoester (**15**) and the iodoester (**16**) cause complications in that the bromo compound gives the 2-substituted product mixed with the internal allylsilane (**17**), whilst the iodoester forms only desilylated products. These side products most probably arise from residual HBr and HI generated during the reaction.



(11) (13)

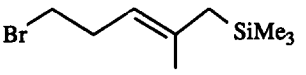


(12) X = Cl

(15) X = Br

(16) X = I

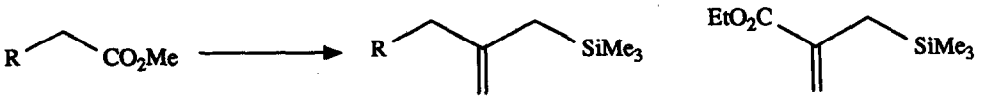
(14) X = Cl



(17)

Other Esters:- Amongst the other 2-substituted functionalised allylsilanes obtainable by this chemistry is the alcohol (**18**) which as its acetate (**19**) underpins a large portion of recent work upon the chemistry of the palladium (0) complex of trimethylenemethane in [3+2] annulations[11]. This improved route to this compound, made directly from trimethylsilyl protected ethyl glycolate, enhances this area of annulation chemistry.

In addition the allylsilanes (**20**) to (**21**) have been prepared in the yields shown from the readily available corresponding esters. Intriguingly only the ester (**22**) was obtained upon reaction with diethyl oxalate i.e. only one of the ester groups underwent reaction. To date we have been unable to convert (**22**) to 2,3-bis(trimethylsilylmethyl)buta-1,3-diene in a second reaction under the normal reaction conditions.



(18) R = OH 55%
(19) R = OAc
(20) R = SPh 39%
(21) R = CH_2SPh 47%

(22) 45%

In conclusion the demonstration that the cerium (111) mediated reaction of trimethylsilylmagnesium chloride with esters can be extended to reaction with a range of functionalised esters means that for the first time useful functionalised allylsilanes are now readily available. This is illustrated by us gaining ready access to the annulating reagents (**1**) to (**3**) for our own work, and by the synthesis of allylsilanes (**7**), (**13**), (**18**), (**20**) and (**22**), each of which has already been shown to be a highly useful synthetic intermediate.

Experimental

All organic solvents were distilled prior to use as listed (tetrahydrofuran and ether, which refers to diethyl ether, from sodium/benzophenone; dichloromethane and triethylamine from calcium hydride; methanol from dimethoxy magnesium; trimethylorthoformate and carbon tetrachloride from potassium hydroxide.) Infra-red spectra were recorded on a Perkin-Elmer 1420 or 881 spectrophotometer, nmr on JEOL PMX 60, GX 270 and GX 400 spectrometers using TMS or $CHCl_3$ as an internal standard, and mass spectra were obtained on a VG9090 mass spectrometer. Reactions involving air and/or moisture sensitive intermediates were performed under a nitrogen atmosphere and magnesium sulphate was used for drying solutions of organic compounds.

PREPARATION OF ESTER ACETALS.

The method of Schreiber[10] was used to prepare these compounds.

GENERAL PROCEDURE FOR THE CERIUM MEDIATED FORMATION OF ALLYLSILANES.

An oven-dried, 3-necked 100 ml round bottomed flask, fitted with a nitrogen line, rubber spectrum, vacuum line and stirrer bar, was thoroughly flushed with dry nitrogen and charged with cerium (III) chloride heptahydrate (30 mmol). The flask was heated under vacuum (1 mmHg) at 150°C for 7 hours with vigorous stirring, resulting in the formation of a white mobile solid. The reaction flask was flushed with nitrogen and allowed to cool to 20°C when dry THF (45 ml) was added to the vigorously stirred anhydrous cerium(III)chloride to form a uniform white suspension, which was left to stir for 2 hours. (It is essential that a true suspension is formed without any signs of coagulation occuring).

During this drying procedure a 3-necked 50 ml flask fitted with a condenser, pressure equalised dropping funnel, a rubber septum and a stirrer bar was charged with magnesium turnings (30 mmol) and the whole apparatus was flame dried under a flow of nitrogen. Chloromethyltrimethylsilane (30 mmol) in dry THF (12ml) was added dropwise under an atmosphere of nitrogen to form a clear grey solution which was stirred for 1.5 hours until all the magnesium was dissolved.

The dry cerium (III) chloride suspension was now cooled to -78°C with stirring and the Grignard reagent prepared above was added dropwise to form an off-white suspension which was stirred at -78°C for 1 hour when the ester (10 mmol) was added dropwise over 5 minutes and the resulting mixture was warmed

gradually to room temperature whilst the reaction was monitored by tlc. When consumption of starting ester was complete the grey solution so formed was cooled to -78°C and quenched by the dropwise addition of 5% hydrochloric acid (16 ml), allowed to warm to 20°C when the organic layer was separated and the aqueous layer extracted with diethylether (2 x 20 ml). The combined organic layers were washed with saturated sodium chloride solution (2 x 25 ml), saturated sodium bicarbonate solution (2 x 25 ml) and dried ($MgSO_4$). The solvent was evaporated *in vacuo* to give a clear yellow liquid which can be purified if required by flash chromatography using diethylether-petrol (5:95) as eluent or by distillation, to afford the alcohol as a colourless oil.

The alcohol (6 mmol) was dissolved in dichloromethane (50 ml) and silica gel (60-120 mesh, 3.06 g) was added. The mixture was stirred at 20°C until tlc indicated complete reaction when the silica gel was filtered off and thoroughly washed with dichloromethane (2 x 25 ml). The solvent was evaporated from the filtrate *in vacuo* to give a clear pale yellow liquid which was purified by flash chromatography using diethylether-petrol (5:95) as eluent or by distillation, to afford the allylsilane as a colourless liquid.

The following allylsilanes were prepared by this method.

ACETAL-ESTERS

3,3-DIMETHOXY-2-(TRIMETHYLSILYLMETHYL)PROP-2-ENE (1)

Trimethylsilylmethyl magnesium chloride (1.90 g; 13.0 mmol), anhydrous cerium (111) chloride (3.24 g; 13.0 mmol) and methyl dimethoxy acetate (0.79 g; 6.0 mmol) were reacted for 18 hrs to give a colourless oil, which after silica treatment and chromatography afforded the acetal (**1**) as a colourless oil (0.45g, 40%).

Found C, 57.12; H, 10.35. $C_9H_{20}O_2Si$ requires C, 57.39; H, 10.70 %; υ_{max} 1635 (C=C)cm^{-1}; δ_H CCl_4, 4.95 (1H, m, vinyl H), 4.75 (1H, m, vinyl H), 4.40 (1H, S, -$CH(OMe)_2$), 3.25 (6H, s, -OMe), 1.68 (2H, s, -CH_2SiMe_3), 0.05 (9H ,s, $SiMe_3$); m/z, 188 (M^+).

2-(TRIMETHYLSILYLMETHYL)PROP-2-ENAL (7)

Prolonged silica treatment of the above tertiary alcohol at reflux temperature in chloroform and distillation gave 0.35g (41%) of the aldehyde (**7**)[10] as a colourless oil (b.p. 50-51°C/0.5 mmHg).

υ_{max} 1680 (C = O)cm^{-1}; δ_H $CDCl_3$, 9.45 (1H, s, CHO), 5.89 (1H, brs, vinyl H), 5.66 (1H, brs, vinyl H), 1.75 (2H, s, CH_2SiMe_3), 0.05 (9H, s, $SiMe_3$); m/z, 142 (M^+).

4,4-DIMETHOXY-2-(TRIMETHYLSILYLMETHYL)BUT-1-ENE (2)

Trimethylsilylmethyl magnesium chloride (2.64 g; 18.0 mmol), anhydrous cerium (111) chloride (4.50 g; 18.0 mmol) and methyl 3,3-dimethoxy propionate (0.88g; 6.0 mmol) were reacted for 2.5 hrs to give 1.22 g of a colourless oil, which after silica treatment and chromatography afforded the acetal (**2**) as a colourless oil (0.58g, 48%).

Found C, 59.75; H, 11.19 , $C_{10}H_{22}O_2Si$ requires C, 59.37; H, 10.96%; ν_{max} 1640 (C = C), 1255 ($SiMe_3$), 860 cm^{-1}; δ_H $CDCl_3$, 4.81 (1H, s, vinyl H), 4.77 (1H, s, vinyl H), 4.51 (1H, m, $CH(OMe)_2$), 3.35 (6H, s, $(OMe)_2$), 2.32 (2H, d, $CH_2CH(OMe)_2$), 1.55 (2H, s, CH_2SiMe_3), 0.015 (94, s, $SiMe_3$); δ_C $CDCl_3$, 142.8, 109.9, 103.7, 52.8, 41.25, 27.1, -1.4; m/z, 187 (M-15, 2%), 171, 155, 147, 115, 105, 75, 73, 67, 59, 45.

PREPARATION OF 7,7-DIMETHOXY-2-TRIMETHYLSILYLMETHYL-HEPT-1-ENE

Trimethylsilylmethyl magnesium chloride (7.32g; 50 mmol), anhydrous cerium (111) chloride (12.47g; 50 mmol) and methyl(6,6-dimethoxy)hexanoate (1.90 g, 10 mmol) were reacted for 12 hrs to give 3.44 g of a colourless oil, which after silica treatment and chromatography afforded the acetal as a colourless oil (1.9g, 78%).

Found C, 64.38; H, 11.49; $C_{13}H_{28}O_2Si$ requires C, 63.93; H, 11.47%; υ_{max} 1635 (C = C); δ_H $CDCl_3$, 4.55 (1H, m, vinyl H), 4.48 (1H, m, vinyl H), 4.34 (1H, t, J=5.7Hz, $CH(OMe)_2$), 3.29 (6H, s, $(OCH_3)_2$), 1.91-1.95 (2H, t, J=7.1 Hz, CH_2), 1.56-1.61 (2H, m, $CH_2CH(OMe)_2$), 1.49 (2H, s, CH_2SiMe_3), 1.30-1.46 (4H, m, CH_2), 0.00 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 147.5 (s), 106.8 (d), 104.5 (t), 52.6 (q), 38.2 (t), 32.4 (t), 27.6 (t), 26.7 (t), 24.3 (t), -0.72 (q); m/z, 244 (M^+), 212, 197, 180, 73.

6,6-DIMETHOXY-2-TRIMETHYLSILYLMETHYL-HEX-1-ENE

Trimethylsilylmethyl magnesium chloride (3.22g; 22 mmol), anhydrous cerium (111) chloride (5.48g; 22 mmol) and methyl 5,5-dimethoxypentanoate (1.76 g, 10 mmol) were reacted for 12 hrs to give 2.15 g of a colourless oil, which did not require silica treatment and on chromatography afforded the acetal as a colourless oil (0.97g, 42%).

Found 230.1702; $C_{12}H_{26}O_2Si$ requires 230.1720; υ_{max} 1630 (C = C), 1245 (Si-CH_3), 1150-1060 (OCH_3); δ_H $CDCl_3$, 4.54-4.64 (1H, m, vinyl H), 4.48 (1H, m, vinyl H), 4.32-4.35 (1H, t, J=5.7Hz, $CH(OMe)_2$), 3.27 (6H, s, OCH_3), 1.87-1.93 (2H, t, J=7.6Hz, $CH_2CH(OMe)_2$), 1.53-1.57 (2H, m, $CH_2CH_2CH(OMe)_2$), 1.48 (2H, s, CH_2SiMe_3), 1.44-1.47 (2H, m, $CH_2(CH_2)CH(OMe)_2$), 0.00 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 147.0 (s), 107.1 (d), 104.4 (t), 52.5 (q), 37.8 (t), 32.0 (t), 26.5 (t), 22.6 (t), -1.4 (q); m/z, 230 (M^+), 198, 183, 73.

ACETAL-ALLYLSILANE (8)

Trimethylsilylmethyl magnesium chloride (4.39g; 30 mmol), anhydrous cerium (111) chloride (7.48g; 30 mmol) and methyl 3-(1',1'-dimethoxymethyl) cyclopentcarboxylate (2.02g, 10 mmol) were reacted for 12 hrs to give a yellow oil, which after silica treatment and chromatography afforded the acetal (**21**) as a colourless oil (1.28g; 54%).

Found: C, 65.49; H,11.50. $C_{14}H_{28}O_2Si$ requires C, 65.63; H, 10.94%; υ_{max} 1630 cm^{-1} (C=C); δ_H $CDCl_3$,4.5 (2H, m, vinyl H), 4.12 (H, d, J=7.88 Hz, $CH(OMe)_2$), 3.31 (6H, s, OMe), 2.27 (2H, brs, CH_2SiMe_3), 1.17-1.93 (8H, m, CH_2), -0.004 (9H, s, $SiMe_3$); m/z, 256 (M^+,3%), 224, 210, 183, 147, 111, 73.

2-(3'-(2'-TRIMETHYLSILYLMETHYL)PROP-1'-ENE)-1,3-DIOXOLE

Trimethylsilylmethyl magnesium chloride (0.65G; 4.4 mmol), anhydrous cerium (111) chloride (1.09g; 4.4 mmol) and methyl 2-1',3'-dioxolylacetate (0.29g, 2 mmol) were reacted for 18 hrs to give a colourless oil, which after silica treatment and chromatography afforded the acetal (**21**) as a colourless oil (0.21g; 53%).

Found: C, ; H,; $C_{11}H_{22}S_2Si$ requires C, 59.95; H, 10.06%; ν_{max} 1635, 1248, 1047, 839 cm^{-1}; δ_H $CDCl_3$, 4.94, (1H, t, OCHO), 4,71 (1H, m, vinyl H), 4.64 (1H, brs, vinyl H), 4.01-3.76 (4H, m, CH_2O), 2.28, (2H, dd, J=5.1,0.9Hz, allylic H), 1.59 (2H, d, J=0.9Hz, CH_2SiMe_3), -0.002 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 142.35, 110.2, 103.7,64.7, 42.65, 27.25, -1.5; m/z, 200 (M^+, 3%), 141, 73.

2-(3'-(2'-TRIMETHYLSILYLMETHYL)PROP-1'-ENE)-1,3-DITHIANE

Trimethylsilylmethyl magnesium chloride (6.17g; 42 mmol), anhydrous cerium (111) chloride (10.37g; 42 mmol) and methyl 2-1',3'-dithianylacetate (1.92g, 10 mmol) were reacted for 18 hrs to give a colourless oil, which after silica treatment and chromatography afforded the acetal (**21**) as a colourless oil (2.35g; 95%).

Found: C, 53.38; H,9.15; $C_{11}H_{22}S_2Si$ requires C, 53.60; H, 9.00%; υ_{max} 1634, 1422, 1249 855 cm^{-1}; δ_H $CDCl_3$, 4.72 (1H, m, vinyl H), 4.65 (1H, s, vinyl H), 4.16 (1H, t, J=7.4Hz, HCS), 2.92-2.72 (4H, m, CH_2S), 2.33 (2H, dd, J=7.5,0.9Hz, allylic H), 2.15-1.71 (2H, m, CH_2), 1,54 (2H, d, J=0.9Hz, CH_2SiMe_3), -0.002 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 142.35, 110.9, 45.5, 43.95, 30.5, 26.2, 25.7, -1.45; m/z, 248 (M^++1,1.5%), 247 (M^++2,2%), 246 (M^+,10%), 231, 173, 157, 119, 99, 73.

LACTONES

2-TRIMETHYLSILYLMETHYL-PENT-1-ENE-5-OL (9)

Trimethylsilylmethyl magnesium chloride (7.32g; 50 mmol), anhydrous cerium (111) chloride (12.47g, 50 mmol) and butyrolactone (1.72 g; 20 mmol) (0.92 9.2 mmol) were reacted for 17 hrs to give 4.00 g of a colourless oil, which did not require silica treatment and on chromatography afforded the alcohol (10) as a colourless oil (2.28 g; 74%).

Found: C, 62.77; H, 11.88. $C_9H_{20}OSi$ requires C, 62.73; H, 11.70%; υ_{max} 3350 (O-H), 3090 (C-H of C=C), 1630 (C=C), 1248 ($SiMe_3$), 1050 (C-O) cm^{-1}; δ_H $CDCl_3$, 4.57 (1H, m, vinyl H), 4.47 (1H, m, vinyl H), 3.57 (2H, t, J=6.6Hz, CH_2OH), 2.53 (1H, brs, OH), 1.98 (2H, bt, J=7Hz, $CH_2(CH_2)_2OH$), 1.65 (2H, m, CH_2CH_2OH), 1.49 (2H, d, J=1Hz, CH_2SiMe_3), - 0.03 (9H, s, $SiMe_3$), δ_C $CDCl_3$, 147.23 (s), 107.20 (t), 62.78 (t), 34.48 (t), 30.66 (t), 26.66 (t), -1.36 (q), m/z, 172 (0.2%, M^+) 157, 73.

2-TRIMETHYLSILYLMETHYLHEX-1-EN-6-OL (10)

Trimethylsilylmethyl magnesium chloride (3.36g; 23 mmol), anhydrous cerium (111) chloride (5.73g; 23 mmol) and valerolactone (0.92 9.2 mmol) were reacted for 19 hrs to give 2.34 g of a colourless oil, which after silica treatment and chromatography afforded the alcohol as a colourless oil (1.02g, 62%).

Found C, 64.89; H, 11.58 %; $C_{10}H_{22}OSi$ requires C, 64.45; H, 11.90%; ν_{max} 1650, 1253, 1105, 840 cm^{-1}; δ_H $CDCl_3$, 4.56 (1H, m, vinyl H), 4.48 (1H, m, vinyl H) 3.60 (2H, t, J=6.3Hz, CH_2OH), 3.59-3.56 (1H, brs, OH),1.95 (2H, brt, allylic CH_2), 1.58 - 1.41 (4H, m, CH_2),1.49 (2H, d, J=0.7Hz, CH_2SiMe_3),-0.02 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 147.3, 107.0, 62.75, 37.9, 32.4, 26.65, 23.9, -1.4; m/z, 186 (M^+, 1%), 171, 129, 96, 81, 75, 73), 68.

CHLORO-ESTERS

3-CHLORO-2-(TRIMETHYLSILYLMETHYL)PROP-1-ENE (13)

Trimethylsilylmethyl magnesium chloride (4.07g; 27.8 mmol), anhydrous cerium (111) chloride (6.93g, 27.8 mmol) and methyl chloroacetate (1.37g, 12.6 mmol) were reacted for 18 hrs to give 4.07g of a colourless oil, which after silica gel treatment and chromatography afforded the chloride (13)[12] as a colourless oil (1.07g; 52 %).

υ_{max} 3083, 1633, 1249, 845 cm^{-1}; δ_H $CDCl_3$, 4.99 (1H, s, vinyl H), 4.75 (1H, s, vinyl H), 3.96 (2H, s, CH_2Cl), 1.68 (2H, s, CH_2SiMe_3), 0.04 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 143.0, 112.3, 49.9, 23.6, -1.5; m/z, 167 (M^++1, 2%), 165 (M^++1, 2%), 164 (M^+,2%), 162 (M^+,9.3%), 147, 129, 111, 95, 93, 86, 73.

5-CHLORO-2-(TRIMETHYLSILYLMETHYL)-PENT-1-ENE (14)

Trimethylsilylmethyl magnesium chloride (7.32g; 50 mmol), anhydrous cerium (111) chloride (12.47g; 50 mmol) and methyl 4-chlorobutyrate (1.37g; 10 mmol) were reacted for 16 hrs to give a colourless oil, which after silica treatment and chromatography afforded the chloride (13) as a colourless oil (1.45 g; 76%).

Found: 190.0960; $C_9H_{19}SiCl$ requires; 190.0945; ν_{max}3070, 1636, 1252, 856 cm^{-1}; δ_H $CDCl_3$, 4.60 (1H, brs, vinyl H), 4.55 (1H, brs, vinyl H), 3.52 (2H, t, J = 6.5 Hz, CH_2Cl) 2.10 (2H, m, allyl CH_2), 1.90 (2H, m, CH_2CH_2Cl) 1.51 (2H, s, CH_2SiMe_3), 0.02 (9H, s, $SiMe_3$); m/z, 192 (M^+, 3%), 190 (M^+, 7%), 139, 128, 95, 93, 73, 67.

OTHER ESTERS

2-TRIMETHYLSILYLYMETHYL PROP-2-EN-1-OL(18)

Trimethylsilylmethyl magnesium chloride (4.07g; 27.8 mmol), anhydrous cerium (111) chloride (6.93g, 27.8 mmol) and ethyl (trimethylsilyloxy)acetate (1.00 g, 5.7 mmol) were reacted for 16 hrs to give 0.69g of a colourless oil, which did not require silica treatment and on chromatography afforded the alcohol (18)[11]as a

colourless oil (0.45g; 55 %).

ν_{max} 3500-3100 (OH), 1650 (C = C), 1245 (Si-CH_3), 860-835 (Si-C). δ_H CCl_4, 4.85 (1H, m, vinyl H), 4.55 (1H, m, vinyl H), 3.85 (2H, s, -CH_2OH), 1.85 (1H, s, -OH), 1.55 (2H, s, CH_2SiMe_3), 0.05 (9H, s, $SiMe_3$).

3-PHENYLTHIO-2-TRIMETHYLSILYLPROP-1-ENE (20)

Trimethylsilylmethyl magnesium chloride (0.74g; 5.1 mmol), anhydrous cerium (111) chloride (1.26 g, 5.1 mmol) and methyl 2-phenylthioacetate (0.42g, 2.3 mmol) were reacted for 18 hrs to give 0.43g of a colourless oil, which after silica treatment and chromatography afforded the thioether (**20**) as a colourless oil (0.21g; 39 %).

ν_{max} 2960, 1625, 1580 cm^{-1}; δ_H $CDCl_3$, 7.23 (5H, m, Ph), 4.75 (1H, brs, vinyl H), 4.59 (1H, s, vinyl H), 3.44 (2H, s, CH_2SPh), 1.68 (2H, brs, CH_2SiMe_3), 0.1 (9H, s, $SiMe_3$); δ_C 143.7, 131.1-127.5 (3C's), 112.6, 43.8, 26.4, 0.1; m/z, 236 (M^+,42%), 221, 164, 73.

4-PHENYLTHIO-2-TRIMETHYLSILYLBUT-1-ENE (21)

Trimethylsilylmethyl magnesium chloride (1.01g; 6.94 mmol), anhydrous cerium (111) chloride (1.73g, 6.94 mmol) and methyl 2-phenylthioacetate (0.62g, 3.15 mmol) were reacted for 18 hrs to give 0.64g of a colourless oil, which after silica treatment and chromatography afforded the thioether (**21**) as a colourless oil (0.37g; 47 %).

Found: 250.4729; $C_{14}H_{22}SSi$ requires; 250.4733; ν_{max} 2930, 1630, 1580 cm^{-1}; δ_H $CDCl_3$, 7.29 (5H, m, Ph), 4.66 (1H, brs, vinyl H), 4.61 (1H, s, vinyl H), 3.03 (2H, t, CH_2PhS), 2.29 (2H, m, CH_2), 1.56 (2H, brs, CH_2SiMe_3), 0.1 (9H ,s, $SiMe_3$); m/z, 250 (M^+, 23%), 235, 73.

ETHYL (2-TRIMETHYLSILYLPROP-2-ENOATE (22)

Trimethylsilylmethyl magnesium chloride (4.68g; 32 mmol), anhydrous cerium (111) chloride (7.98g, 32 mmol) and diethyl oxalate (0.87g, 6 mmol) were reacted for 18 hrs to give 1.62g of a colourless oil, which after treatment with boron trifluoride etherate (6 mmol)and chromatography afforded the ester (**22**)[11]as a colourless oil (0.50g; 45 %).

Found: 186.3068; $C_9H_{18}O_2Si$ requires; 186.3255; ν_{max} 2900, 1720, 1620; δ_H CCl_4, 5.97 (1H, brs, vinyl H), 5.29 (1H, s, vinyl H), 4.19 (2H, q, OCH_2), 1.85 (2H, s, CH_2SiMe_3), 1.29 (3H, t, OCH_2CH_3), 0.01 (9H, s, $SiMe_3$); δ_C 169.4, 140.5, 123.2, 62.4, 24.0, 16.0, 0.0; m/z, 186 (M^+, 8%), 171, 143, 73.

5,5-DIMETHOXY-2-TRIMETHYLSILYLMETHYL-PENT-1-ENE (3)

4-TRIMETHYLSILYLMETHYLPENT-4-ENAL:- Dry dimethylsulphoxide (1.08g) was added dropwise under nitrogen at -78°C to a stirred solution of freshly distilled oxalyl chloride (0.88g) in dry dichloromethane (25ml). After 30 mins the alcohol (**9**) (0.80g) in dichloromethane (5ml) was added dropwise to the solution and the resultant creamy mixture stirred at -78°C for 1.2h. Triethylamine (2.93g) was added rapidly and the reaction warmed to room temperature over 30 mins when water (20ml) and dichloromethane (20ml) were added and the organic phase separated, washed with 2M aqueous sulphuric acid (15ml), saturated sodium hydrogencarbonate solution (10ml) and water (10ml) and dried ($MgSO_4$). Evaporation yielded an aldehyde (0.73g, 92%) as a yellow oil. R_F (Et_2O) 0.69, which was not purified further. υ_{max} (neat) 1720 (C=O), 1635 (C=C), 1250 ($SiMe_3$) and 850 cm^{-1} (Si-C); δ_H $CDCl_3$, 9.75 (1H, t, J=1.7Hz, -CHO), 4.54 (2H, brs, vinyl H), 2.55 (2H, d of t, J=1.7 and 7Hz, CH_2CHO), 2.26 (2H, t, J=7Hz, CH_2CH_2CHO), 1.51 (2H, s, CH_2SiMe_3), 0.00 (9H, s, $SiMe_3$); δ_C $CDCl_3$, 201.53 (d), 145.18 (s), 107.30 (t), 42.08 (t), 30.52 (t), 27.37 (t), -0.97 (q).

Alternative oxidation of the alcohol (8) using silver carbonate on celite:- A mixture of the alcohol (**9**) (0.10g) and silver carbonate on celite (2.4g, 6 equivalents) in dry benzene (10ml) was heated at reflux under