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THE PREPARATION AND REACTIONS WITH AN O-SILYLATED ENOLATE OF AN ALLYLSILANE BIFUNCTIONAL [3 + 2] ANNULATING REAGENT

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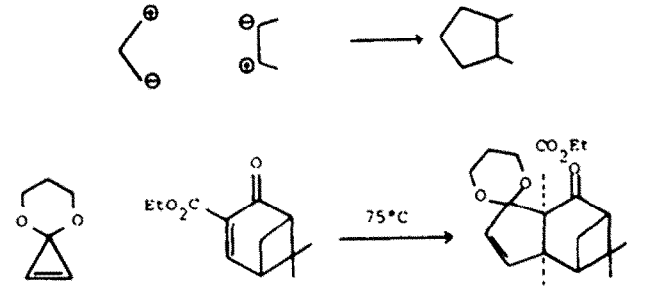
Summary: The preparation and reactions of allylsilane-acetal (13) with various silyl enol ethers are described. This results in the one-pot synthesis of fused and spiro cyclopentanes by using a 1,3-bifunctional annulating reagent in which the two reactive centres are activated by one set of conditions.

Introduction

The structural elucidation of a range of quinane and polyquinane based natural products such as the prostaglandins[1], ophiobolins[2] and the iridoids[3] has led, in the last ten to fifteen years, to the development of a number of different methods for the synthesis of five-membered rings[4]. However by comparison to the preparation of cyclohexanes, which is dominated by the powerful Diels-Alder strategy, access to five-membered rings has been limited. It has therefore become apparent that a cycloaddition strategy to cyclopentanes would be of great value and a number of groups have reported upon their efforts to achieve a general [3 + 2] annulation reaction. (SCHEME 1).

(SCHEME 1)



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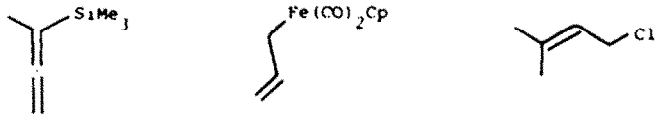
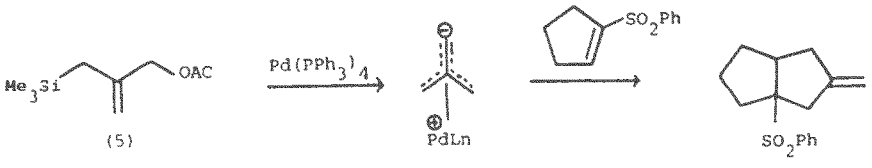


(2) (3) (4)

Amongst the most interesting of these is the use of the cyclopropenone ketal (1) in its reaction with an electron deficient alkene, whereby the reaction is thought to proceed via a 1,3-dipole.[5] Other reagents which have proved useful include the allenylsilane (2),[6] the allyliron complex (3),[7] and the allylic chloride (4),[8] with the former two again undergoing cyclization with

electron deficient alkenes and the latter reacting with alkynes.

However the most powerful strategy yet reported involves controlled reactions of trimethylenemethane. This has resulted in the development of a method whereby a zwitterionic equivalent of trimethylenemethane is generated by formation of a palladium (0) complex from the allylsilane (5).[9] This then undergoes a facile reaction with a range of electron deficient



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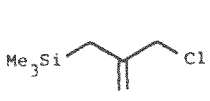

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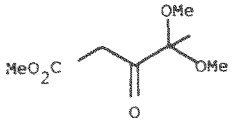

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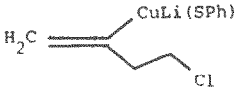

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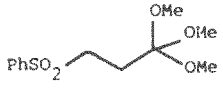
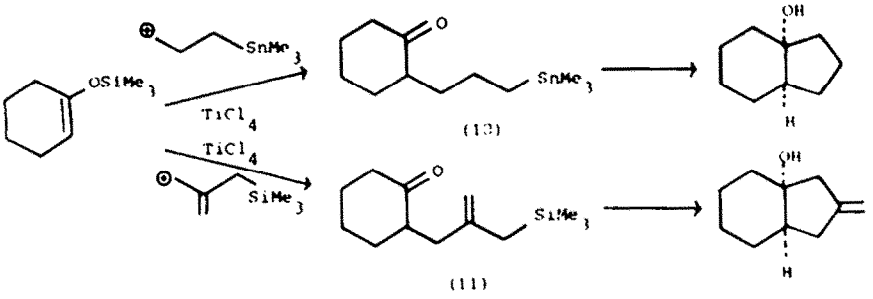


(9)

alkenes. As has been pointed out by Trost, the originator of this work, the essence of this reaction lies in the compatibility of the allylsilane and acetate within the same molecule. These two centres, one nucleophilic and one electrophilic, do not self-destruct but do require activation, provided for them by the palladium catalyst. These type of compounds have been christened as 1,3-bifunctional conjunctive reagents and are epitomised by this compatibility of the two potentially reactive functions. Others have addressed this problem by selecting the reactive functions such that they require activation under two sets of different and incompatible conditions. Thus the allylsilane (6),[10] the β-keto ester (7),[11] the cuprate (8)[12] and the orthoester (9)[13] have all been shown to react in the same sense as the trimethylenemethane complex but they are not 1,3-dipolar species and so require two reactions to achieve an overall [3 + 2] annulation process. This is unfortunate since in terms of yield and generality of the electron deficient alkene substrates, the trimethylenemethane complex possesses some limitations (unsubstituted enones for example, react very poorly). Therefore compounds such as those described above may offer some advantages. A useful compromise would be to develop a bifunctional annulating reagent in which the two centres can be activated by one set of conditions but in a controlled, sequential manner. If properly designed such a species could maintain the one-pot feature of the 1,3-dipolar trimethylenemethane whilst possibly providing the more reactive features of the reagents (6)-(9). This current paper discusses one way in which this may be achieved by use of a 1,3-bifunctional conjunctive reagent, which does not form a dipolar species, but for which the electrophilic and nucleophilic centres can be activated sequentially under one set of conditions.

One of the features of organosilicon compounds is the ability to carry the silicon group through a wide range of transformations prior to using the inherent reactivity of the silicon functionality. It is not surprising therefore that this feature, which is used in the generation of the Trost trimethylenemethane chemistry, is the basis for the controlled reactions which we have developed to address the problems outlined above.

Precedents for the Lewis acid catalysed cyclisation of ketones such as (10) was reported in 1980.[14] If it were possible to form this ketone directly by reaction of an O-silylated enolate with some electrophilic species an annulation under one set of conditions would be feasible.



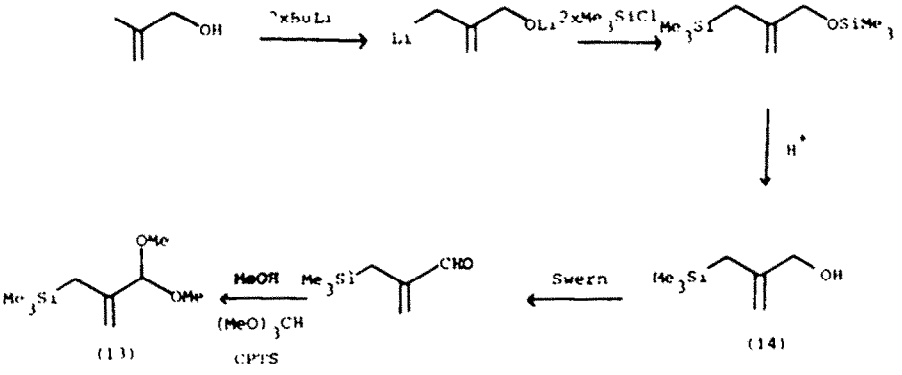
(13) (11)

(12) (13)

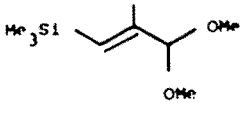
Similarly an allylsilane based electrophile (11) could be used to give an even more useful cyclopentane product. We have already reported upon the use of the stannane (12) in this way[15] and have briefly described some reactions of the allylsilane (13).[16] Now these silicon based reagents can be used in a controlled manner will now be described.

Results and Discussion

The synthesis of the allylsilane (13) is outlined in SCHEME 2 and involves the preparation of the alcohol (14) as described by Trost. Thus formation of the dianion of methallyl alcohol and quenching with two equivalents of chlorotrimethylsilane gave a bis-silyl compound which upon

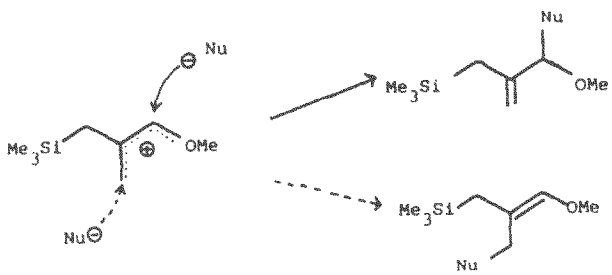


(13) (14)

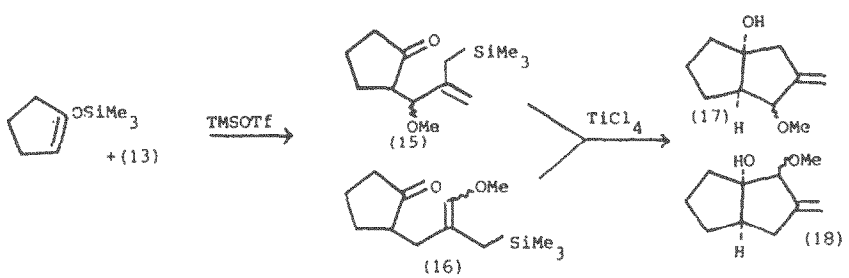


careful hydrolysis provided the alcohol (14).[17] Oxidation to an aldehyde under Swern conditions was then followed by acetal formation using methanol and trimethylorthoformate in the presence of collidinium p-toluenesulphonate.[18] The use of stronger acid catalysts results in an appreciable degree of protiodesilylation and so should be avoided. On occasions the allylsilane (13) was contaminated with small amounts of the corresponding vinylsilane (15) which had carried through from the lithiation reaction[17]. These two compounds are easily separated using flash chromatography.

Upon activation by Lewis acid the electrophilic acetal centre of (13) forms an unsymmetrical



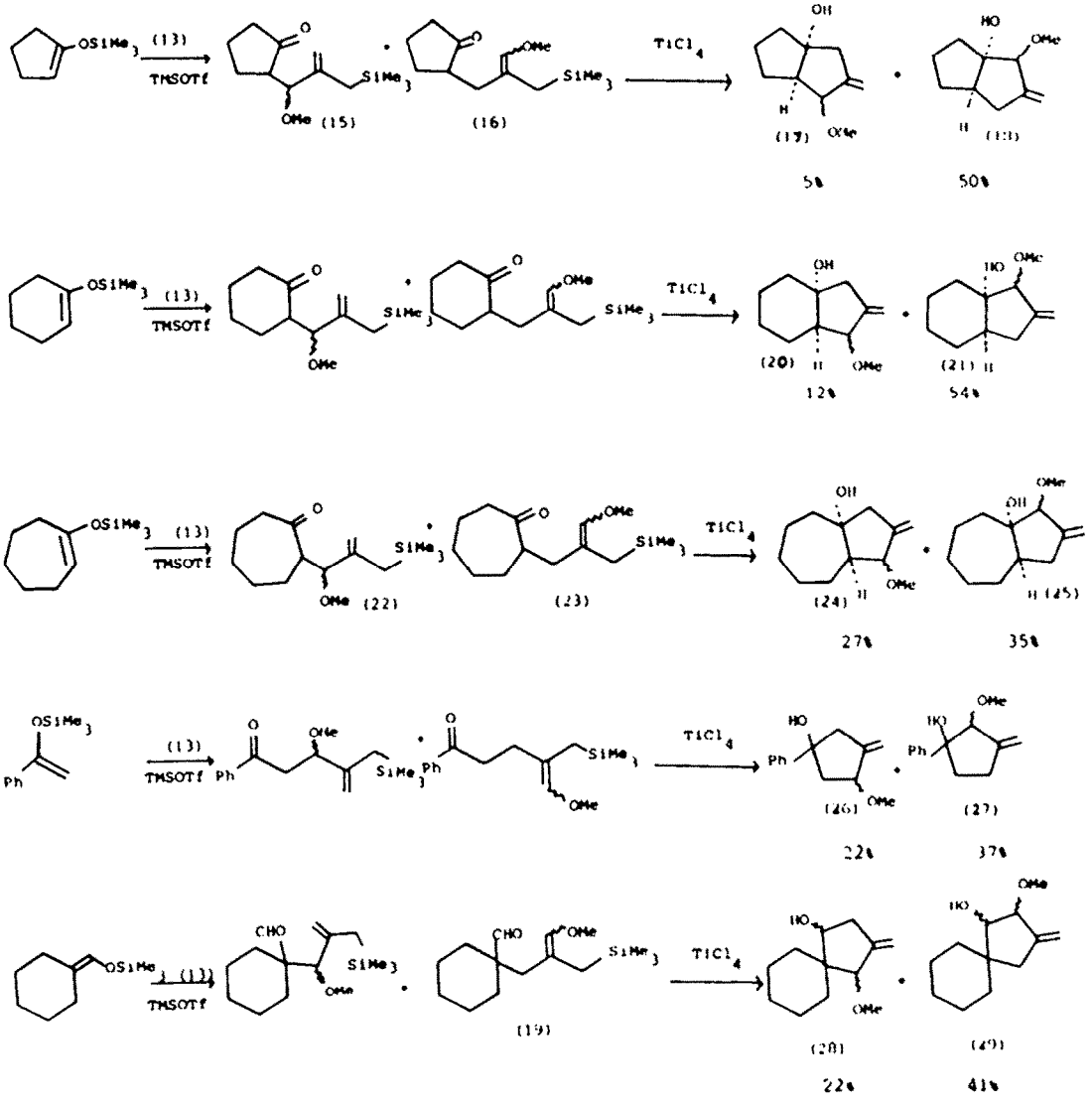
allylic cation which can undergo nucleophilic attack at two alternative sites. Therefore the allylsilane (13) can be expected to lack total regiocontrol in its initial reaction. Upon reaction with the O-silylated enolate of cyclopentanone in the presence of trimethylsilyltrifluoromethanesulphonate, two intermediates are formed, the allylsilane (15) and the enol-allylsilane (16).



It was not possible to separate these two compounds by chromatography and normally the reaction was taken through to completion without isolation of the intermediates by the addition of titanium tetrachloride to give the bicyclic alcohols (17) and (18), in an overall yield of 68%. However a close examination of this cyclization step revealed some interesting features which have reduced the problem of lack of regioselectivity. The two ketones (15) and (16) cyclize at different rates at -78°C, such that total reaction of (16) occurs before any of (15) reacts. No cyclization of (15) is seen except after prolonged periods or if the reaction mixture is warmed to -20°C. The two products of reaction at -78°C (17) and (18) are readily separated chromatographically so allowing the removal of the minor regioisomer (15) which is formed in 7% yield.

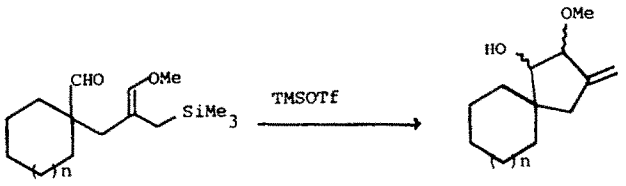
These features of regioisomer formation, selective cyclization and chromatographic separation are repeated throughout all of the examples attempted, as listed in the TABLE. The most important feature of the results shown is the variation with the enol structure of

TABLE



the ratio of the two initially formed intermediates, arising from allylic or direct attack at the unsymmetrical allylic cation. By using the rate differences for cyclization there is no difficulty in separating the two products. However although both the five and six-membered ring enols give mainly the product arising from allylic attack, and so are synthetically useful, the other enols used give no selectivity. Additionally we have not yet demonstrated any large degree of stereocontrol during attack at the acetal centre. This is in marked contrast to the previously reported tin analogy to this work in which we can achieve total control of stereochemistry at what was initially the acetal carbon.[15]

The reaction with the carboxaldehyde derived enol is additionally interesting since the cyclization stage involving attack at an aldehyde (19) occurs spontaneously in the presence of TMS-OTf, for the aldehyde derived from allylic attack, so simplifying the process and allowing



(19)

separation of the two isomers. The rate difference in cyclization presumably reflects the greater nucleophilicity of the allylsilane in which the alkene is part of an enol ether. The presence of the methoxy group in both cyclization products and the ring size shows that cyclization of such as (19) does involve an allylsilane and not attack by the enol ether.

Although this new cyclopentannulation reaction is not as useful synthetically as the complementary tin reaction we have described[15] it does appear to be useful in reactions with some enols. However it does demonstrate the principle that we set out to establish. It is possible to design a 1,3-bifunctional reagent containing an electrophilic and nucleophile centre in which the two centres can be activated by one set of conditions in a controlled sequential manner. The regiochemical limitations do not detract from this principle since both regioisomers are obtained via this controlled process. Furthermore higher homologues of (13) in which the allylsilane and the acetal are separated by methylene groups will not suffer from the formation of an unsymmetrical allylic cation and we are currently successfully extending this concept to the synthesis of six and seven-membered rings.

In conclusion this work extends the idea of using a reactive bifunctional reagent in ring formation to a system in which two potentially self destructive centres are activated by the same set of conditions and yet will undergo a controlled and chemoselective reaction. This illustrates graphically the degree of control available by using organosilicon chemistry.

Acknowledgement: We would like to thank SERC for support of this work.

Experimental

Tetrahydrofuran was distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. TMEDA was distilled under reduced pressure from potassium hydroxide. Triethylamine was distilled from calcium hydride. Ether refers to diethyl ether which was distilled before use. Methanol was distilled from sodium, trimethylorthoformate was distilled from potassium hydroxide. Carbon tetrachloride was distilled from potassium hydroxide. Infra-red spectra were recorded on a Perkin-Elmer 1420 spectrophotometer, nmr on a JEOL PMX60 and GX270 spectrometers using TMS or CH_2Cl_2 as an internal standard, and mass spectra were obtained on a VG9090 mass spectrometer. Magnesium sulphate was used to dry solutions of organic compounds.

(2-(Trimethylsilyloxy)methyl)3-allyl) trimethylsilane[17]

Following a known procedure[17], into an over-dried, N_2 flushed 3-necked 2l round bottomed flask, fitted with outlet to vacuum, inlet to N_2, a rubber septum and a stirrer bar, was placed n-butyllithium(10.2M; 96ml) (CAUTION). Application of a vacuum, with the N_2 line closed, removed all of the hexane within 30 mins. The viscous oil was cooled in an ice-salt bath, after closure of the vacuum line and opening of the N_2 line, and ether (540ml) was added via a cannula. TMEDA (160ml) was added via a cannula, followed by 2-methyl-propen-1-ol (40ml; 48mmol) over 20 min. To the cloudy yellow reaction mixture was added THF (240ml) via a cannula. The mixture was left to warm to 20°C during 3h, and then left to stir at 20°C for 36h. Trimethylchlorosilane (260ml; 205mol) was added at 0°C with vigorous shaking. Manual shaking was continued until the gummy, red dianion was consumed, after about 0.5h. The resultant yellow solution and grey precipitate was poured into ether (2.5l) and extracted sequentially with saturated sodium hydrogen carbonate solution (1l), water (1l), saturated copper (II) sulphate solution (2 x 1l), water (400ml) and brine (1l). The ethereal layer was dried ($MgSO_4$) and the solvent removed in vacuo (water bath temperature <45°C) to give an orange liquid.

This liquid was distilled under reduced pressure to give a colourless liquid (50.3g, 48%) b.p. 64.66°/1.4mm Hg. ν_{max} 1645(C=C), 1240 (Si-CH_3), 1090 (C-O); δ, CCl_4, 0.020 (s, 9H, $SiMe_3$), 0.10 (S, 9H, $OSiMe_3$), 1.4 (s, 2H, CH_2-$SiMe_3$), 3.80 (br s , 2H, CH_2O), 4.40 (br s, 1H, olefinic H), 4.70 (br s, 1H, olefinic H).

A minor set of signals (≤10%) are sometimes seen and may be assigned to the vinylsilane (15), δ, CCl_4, 0.02 (s, 9H, $SiMe_3$, 0.10 (s, 9H, $OSiMe_3$) 2.00 (s, 3H, CH_3) 3.95 (br s, 2H, CH_2 $OSiMe_3$), 4.90 (br s, 1H, olefinic H).

(2-(Hydroxymethyl)-3-allyl trimethylsilane (14)

The silyl ether (50.0g; 233 mmol) was dissolved in THF (500ml) and stirred vigorously with 1N sulphuric acid (110ml) for 0.5h when potassium carbonate was added until effervescence ceased. The mixture was poured into ether (1.6l) and washed with sodium hydrogen carbonate solution (400ml) and brine (500ml). The ethereal layer was dried ($MgSO_4$) and the solvent removed in vacuo to give an orange, liquid, the alcohol (14) (26.5g; 80%), which was used crude.

δ, CCl_4, 0.05 (s, 9H, $SiMe_3$), 1.45 (br s, 2H, CH_2 $SiMe_3$), 3.75 (br s, 2H, CH_2OH) 4.40 (brs, 1H, olefinic H), 4.70 (br s, 1H, olefinic H); ν_{max} 3300 (OH), 1650 (C=C); m/z 144 (M^+, 32%).

(2-(Carboxaldehyde)-3-allyl)trimethylsilane

Into an oven-dried, N_2 flushed, 3-necked, 1l round-bottomed flask, fitted with a N_2 line, rubber septum, vacuum line and stirrer bar, was placed oxalyl chloride (18.4ml; 211mmol). (It is essential that the oxalyl chloride is distilled immediately prior to use, otherwise yields are reduced) in dichloromethane (450ml). The solution was cooled to -78°C and dimethylsulphoxide (31.3ml; 442mmol) in dichloromethane (90ml) was added via a cannula over 10 min. The reaction was stirred at -78°C for 15 min when the crude alcohol (26.5g; 184mmol) in dichloromethane (120ml) was added over 15 min. The solution was stirred at -78° for 70 min when triethylamine (130ml) was added rapidly. The white suspension was stirred for 2h as the reaction warmed to 20°. Water (100ml) was added, the organic layer was separated and the aqueous layer washed with dichloromethane (80ml). The combined organic layers were washed with 1N sulphuric acid (150ml), saturated sodium hydrogen carbonate solution (150ml) and brine (150ml), and then dried ($MgSO_4$) and evaporated in vacuo to give a green liquid (24.1g, 92%). Vacuum distillation gave a colourless oil (15.6g; 60% b.p. 50-51°C/0.5mmHg. ν_{max} 1680 (C=C), 1250 (Si-CH_3); δCCl_4, 0.05 (9H, s, $SiMe_3$), 1.75 (2H, s,

CH_2-$SiMe_3$), 5.70 (1H, m, olefinic H), 9.45 (1H, s, CHO); m/z 142 (M^+). Found C, 58.87; H, 9.85; $C_7H_{14}OSi$ requires C, 59.09; H, 9.91%.

(2-(Dimethoxymethyl)-3-allyl)trimethylsilane (13)

The aldehyde (24.0g; 169mmol) was dissolved in trimethylorthoformate (20ml) and methanol (40ml). Collidinium p-toluenesulphonate (200mg) was added and the reaction was stirred at 20° for 0.5h. Saturated sodium hydrogen carbonate solution (200ml) was added and the mixture extracted with ether (2 x 100ml). The ethereal layers were washed with brine (100ml), dried ($MgSO_4$) and evaporated *in vacuo* to give an oil (31.5g) which was purified by flash chromatography using ether/petroleum ether (2:98) as eluent, to afford 22.8g (72%) of the allylsilane (13) as a colourless oil.

ν_{max} 1635 (C=C); δCCl_4, 0.05 (9H, s, $SiMe_3$), 1.68 (2H, s, CH_2-$SiMe_3$), 3.25 (6H, s, OCH_3) 4.40 (1H, brs, $CH(OMe)_2$), 4.75 (1H, m, olefinic H), 4.95 (1H, m, olefinic H); m/z, 188 (M^+). Found C, 57.12; H, 10.35; $C_9H_{20}O_2Si$ requires C, 57.39; H 10.70%.

General Procedure for the Reaction of 1,1-Dimethoxy-2-trimethylsilylmethylprop-2-ene (13) and O-Silylated Enolates

A dry, N_2 flushed, 3-neck flask, fitted with a pressure equalised dropping funnel, rubber septum, nitrogen inlet and stirrer bar was charged with the O-silylated enolate (5mmol), allylsilane (6mmol) and dichloromethane (12ml). The solution was cooled to -78°C and TMSOTf (0.05ml) in dichloromethane (2ml) was added with stirring. After 30 min. a small sample was removed, quenched with H_2O and analysed by nmr and glc* to determine the ratio of direct to allylic substitution. The remainder of the solution was treated, at -78°, with $TiCl_4$ (0.56ml; 1.7 mmoles) in dichloromethane (2ml) and stirred at -78°C to -20°C for 3hr when H_2O (3ml) was added, followed by vigorous stirring for 30 min. The aqueous layer was washed with dichloromethane (20ml) and the combined organic layers were washed with brine (10ml), dried and evaporated to give a yellow oil. The two cyclized products were separated by automated flash chromatography using mixtures of ethyl acetate/petroleum ether as eluent.

Alternatively after addition of $TiCl_4$ the solution was stirred at -78°C for 60 mins followed by a similar work up to afford a mixture of two products (one cyclized) which can again be separated by chromatography. Work up prior to the addition of $TiCl_4$ permits isolation of the cyclization precursors, for use as glc standards. By this method the following annulations were performed:-

a) In a representative example the reaction of 1-trimethylsilyloxycycloheptene and the allylsilane (13) was worked up prior to $TiCl_4$ addition to give:-

   (i) Ketone (22) 31% ν_{max} 1710, 1620 cm^{-1}, $\delta(CDCl_3)$, 0.05 (9H, s, $SiMe_3$). 1.05 - 2.3 (13H, m, alkyl), 3.1 (3H, s, OMe), 3.75 (1H, brd, CHOMe), 4.70 (2H, brs, olefinic H); m/z, 268(M^+). Found M^+268.4685 $C_{15}H_{28}O_2Si$ requires M^+ 268.4695.

   (ii) Ketone (23) 37% ν_{max} 1720, 1650 cm^{-1}, $\delta(CDCl_3)$, 0.10 (9H, s, $SiMe_3$), 1.1 - 1.9 (10H, m, alkyl), 2.0 - 2.25 (5H, m, allyl and α-H), 3.45 (3H, s, OMe), 5.60 (1H, brs, olefinic H); Found M^+268.4690 $C_{15}H_{28}O_2Si$ requires M^+ 268.4695.

b) The reactions below were worked up after reaction with $TiCl_4$ for 3hrs from -78° to -20°C.

   (i) (13) + 1-Trimethylsilyloxycyclopentene.
   Alcohol (17), 4.9% ν_{max} 3420(OH)cm^{-1}; δ $CDCl_3$, 1.4 - 2.0 (7H, m, alkyl), 2.1 - 2.3

(2H, brs, allylic), 2.82 (1H, brs, OH), 3.6 (3H, s, OMe), 3.8 (1H, m, CHOMe), 5.52 (2H, s, olefinic H); Found M^+ 168.2325; $C_{10}H_{16}O_2$ requires M^+ 168.2344.

Alcohol (18), 50%. ν_{max} 3400, 1615cm^{-1}; $\delta(CDCl_3)$, 1.4-2.0 (6H, m, alkyl), 2.3-2.25 (3H, m, allylic and CH), 2.35 (1H, brs, OH), 4.0 (4H, brs, OMe and CHOMe), 5.50 (2H, brs, olefinic H). m/z, 168 (M^+, 38%). Found C, 71.25; H, 9.88; $C_{10}H_{16}O_2$ requires C 71.39; H, 9.58.

(ii) (13) + 1-Trimethylsilyloxycyclohexane.

Alcohol (20), 12%. ν_{max} 3380cm^{-1}. $\delta(CCl_4)$ 1.4-2.3 (11H, m, alkyl), 3.1 (1H, brs, OH), 3.5, s, OMe), 3.65 (1H, brs, CHOMe), 4.9 (1H, s, olefinic), 5.05 (1H, brs, olefinic). Found M^+ 182.2635, $C_{11}H_{18}O_2$ requires 182.2612.

Alcohol (21), 54%. ν_{max}, 3400, 1670cm^{-1}; $\delta(CCl_4)$ 1.4-2.3 (11H, m, alkyl), 3.25 (1H, brs, OH), 3.5, s, OMe), 3.80 (1H, brs, CHOMe), 4.85 (1H, brs, olefinic), 5.00 (1H, brs, olefinic); m/z, 182 (M^+). Found C, 65.67; H, 9.80; $C_{11}H_{18}O_2$ requires C, 65.90; H, 9.95.

(iii) (13) + 1-Trimethylsilyloxycycloheptene

Alcohol (24), 27%, ν_{max} 3400, 1615cm^{-1}; $\delta(CCl_4)$ 1.05-2.3 (13H, m, alkyl), 2.65 (1H, brs, OH), 3.20 (3H, s, OMe) 3.35 (1H, m, CHOMe), 4.65 (2H, m, olefinic); Found M^+ 196.2881; $C_{12}H_{20}O_2$ requires 196.2885.

Alcohol (25), 35%. ν_{max} 3400, 1615 cm^{-1}. $\delta(CCl_4)$, 1.10-2.2 (13H, m, alkyl), 2.5 (1H, brs, OH), 3.22 (1H, brs, CHOMe), 3.30 (3H, s, OMe, 4.60 (2H, brs, olefinic); m/z, 196 (M^+). Found C73.21; H, 10.15; $C_{17}H_{20}O_2$ requires C, 73.42; H, 10.27.

(iv) (13) + 1-phenyl-1-trimethylsilyloxyethene

Alcohol (26), 22%. ν_{max}, 3400cm^{-1}; $\delta(CDCl_3)$ 1.75 (2H, t, J = 6Hz, CH_2) 2.20 (2H, t, J = 6Hz, allylic), 2.30 (1H, brs, OH), 3.15 (3H, s, OMe), 3.6 (1H, brs, CHOMe), 5.15 (2H, brs, olefinic), 7.22 (5H, m, aryl). Found M^+ 204.2664; $C_{13}H_{16}O_2$ requires M^+ 204.2674.

Alcohol (27), 37%, ν_{max} 3400cm^{-1}, $\delta(CDCl_3)$ 1.7 (2H, t, J = 6.5Hz, CH_2), 2.25 (2H, brt, J = 6.5Hz, allylic), 2.8 (1H, brs, OH), 3.00 (3H, s, OMe), 3.50 (1H, brs, CHOMe), 5.00 (2H, brs, olefinic), 7.2 (5H, m, aryl). m/z; 204 (M^+). Found M^+204.2655; $C_{13}H_{16}O_2$ requires M^+ 204.2674.

(v) (13) + 1-Trimethylsilyloxycyclohexylidene

Alcohol (28), 22%, ν_{max}, 3500, 1620cm^{-1}; $\delta(CCl_4)$ 1.14-2.1 (10H, m, alkyl) 2.35 (2H, m, allylic), 3.3 (3H, s, OMe), 3.5 (1H, m, CHOH), 3.85 (1H, brs, CHOMe), 4.95 (2H, m, olefinic); m/z 196 (M^+).

Alcohol (29) 41%, ν_{max}, 3500, 1620cm^{-1}; $\delta(CCl_4)$ 1.15-2.15 (10H, m, alkyl), 2.2-2.4 (2H, m, allylic), 2.82 (1H, brs, OH), 3.35 (3H, s, OMe), 3.55 (1H, m, CHOH), 3.85 (1H, brs, CHOMe), 4.95 (2H, brs, olefinic). m/z; 196 (M^+). Found C, 73.15; H, 10.21; $C_{12}H_{20}O_2$ requires C, 73.42; H, 10.27.

* GLC conditions: 7% Dexsil 300GC on 80-120 mesh Gaschrom Q (1m). Oven temperature 210°C.

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