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CYCLOPENTANOID ALLYLSILANES IN SYNTHESIS: GENERATION VIA INTRAMOLECULAR ENE REACTION OF ACTIVATED 1,6-DIENES AND APPLICATION TO THE SYNTHESIS OF FUNCTIONALIZED DIQUINANES

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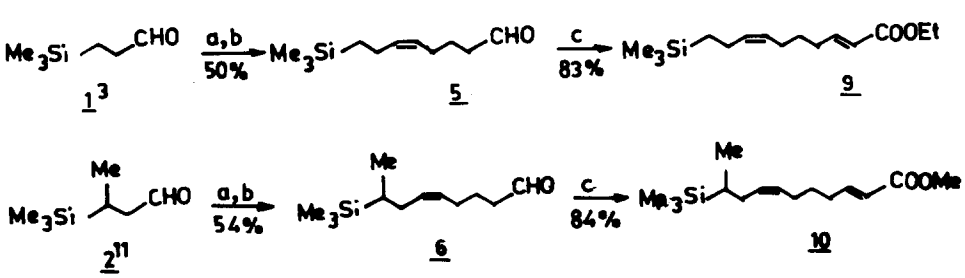
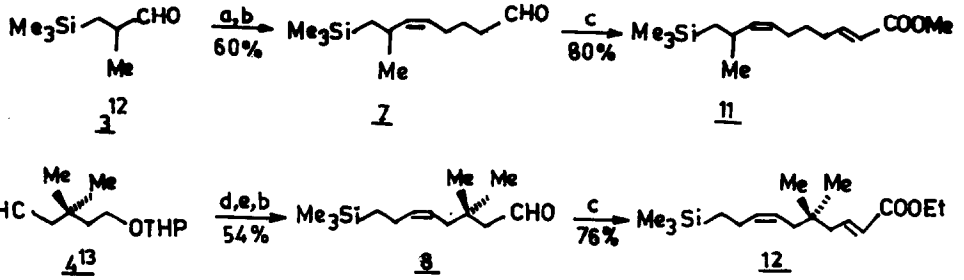
Summary : A new general route to cis-1,2-disubstituted cyclopentanoid allylsilanes useful in di-and triquinane synthesis is described based on intramolecular ene reaction of activated 1,6-dienes featuring a homoallylsilane unit as the ene donor.

Allylsilanes are versatile compounds with well documented utility in organic synthesis.[1] Thus, general methods[2] for the development of these species in which suitable electrophiles are incorporated for use in carbocyclization reactions leading to complex molecules are valuable. In continuation of our work in this area[3,4] we now report a new general route to cis-1,2-disubstituted cyclopentanoid allylsilanes by type I intramolecular Alder ene[5] reaction of suitably substituted 1,6-dienes featuring a homoallylsilane[6] unit as the ene donor. This investigation was prompted by the following considerations : (a) in contrast to inter-and intramolecular Diels-Alder reactions which have been used by various groups[7] for the synthesis of functionalized allylsilanes, the ene reaction which entails high levels of stereoselectivity has never been exploited for the synthesis of allylsilanes,[8,9] and (b) although the ene reactions generally require elevated temperatures for success, these seldom exceed 500°C at which substituted allylsilanes are known to undergo scrambling by rapid 1,3-sigmatropic shifts.[10] Thus, allylsilanes should survive the ene reaction conditions.

The activated 1,6-dienes 9 - 12 used in this study were synthesized following standard synthetic techniques as summarized in Scheme I.

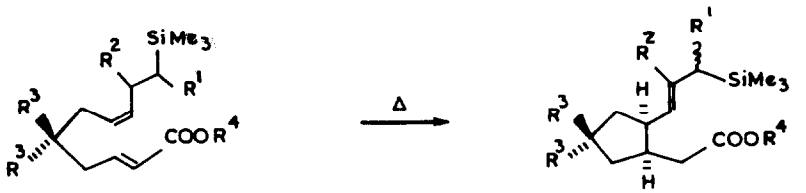
Scheme I[23]





(a) $NaOCH_2(CH_2)_3CH{=}PPh_3$ (13), THF, -78°C (ref. 14); (b) PCC/NaOAc/CH_2Cl_2, r.t; (c) DME, $(EtO)_2P(O)CH(Na)COOEt$ or $(MeO)_2P(O)CH(Na)COOMe$, r.t., then separation of the E:Z-mixture (97:3) by PLC; (d) $Me_3Si(CH_2)_3PPh_3Br$ (14)[15], $NaN(SiMe_3)_2$, THF (ref. 16); (e) PTS/MeOH

Preparative cycloadditions ($\pi 2_s + \sigma 2_s + \pi 2_s$) were carried out in sealed ampoules under argon using a 5% solution of 9-12 in toluene (Table 1). As shown in the table the expected ene reactions occurred smoothly leading to the allylsilanes 15, 16 and 18 in near quantitative yields. However, 11 remained unchanged under these conditions and thwarted all attempts at its cycloaddition even at elevated temperatures for longer reaction periods.



9-12 15-18

Table - 1. Homoallylsilanes to Allylsilanes Conversion Via Ene Reaction.

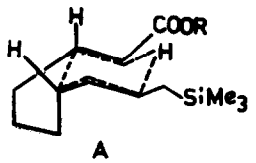
Educt	R^1	R^2	R^3	R^4	Reaction Conditions[a]	Product	Yield[b, 23] [%]
9	H	H	H	Et	252°C/45h	15	98
10	Me	H	H	Me	243°C/16h	16	93
11	H	Me	H	Me	243°C/16h	17	0
12	H	H	Me	Et	245°C/30h	18	97

[a] Reactions were not monitored except in the case 10 to 16.

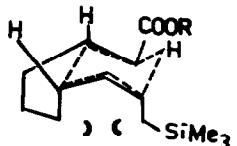
[b] Isolated yield after distillation of crude product.

The stereochemistry of 15, 16 and 18 rests on high-field ^{1}H-NMR as well as some chemical transformations (vide infra). 15 and 18 are essentially free from any of their stereoisomers (^{1}H- & ^{13}C-NMR, GC-MS), whereas 16 is a mixture (~1 : 1 from ^{13}C-NMR) of diastereomers. The geometry of the allylsilane unit in all these compounds (15, 16 & 18) is exclusively E (^{1}H-NMR). This is noteworthy since literature information indicating preference for the formation of E-olefins in intramolecular ene reactions is sparse.[17]

The exclusive formation of E-allylsilanes 15, 16 and 18 is accountable in terms of the relevant transition states,[18] e.g. A which is favoured over B due to 1,3-diaxial interaction. The recalcitrance of 11 towards cycloaddition is presumably due to the unavoidable 1,3-diaxial interaction which results by introduction of the methyl group β to the TMS-group (in A).



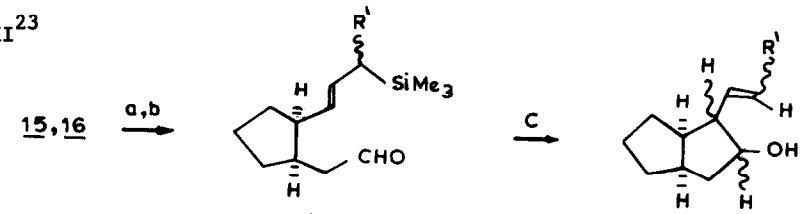
A



B

The results of this study indicate that the method[19] is a convenient route to cis-1, 2-disubstituted cyclopentanoid allylsilanes which are difficult to prepare by other routes. As shown in Scheme II the allylsilanes e.g. 15 & 16 are useful for ready transformation into functionalized diquinanes[22] 21 & 22, respectively. The accompanying paper shows the utility of 18 in a synthesis of the fungal metabolite (±) - hirsutene.

Scheme II[23]



19, R' = H (65%)
20, R' = Me (55%)
21[20], R' = H (70 %)
22[21], R' = Me (80%)

(a) LAH ; (b) $CrO_3.2Py/CH_2Cl_2$ (for 20) & PDC/CH_2Cl_2 (for 19) ; (c) $TiCl_4$, -80°C

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13. Prepared from 3,3-dimethylpentane-1,5-diol via the mono-OTHP ether (45%; yield further improved by recycling the recovered diol) and Swern oxidation (80%) of the latter.

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15. M. P. 239-240°C; obtained in 50% overall yield from 3-trimethylsilyl-1-propanol (ref. 3) via the bromide. See, also : Hetanaka, I.; Kuwajima, I. Tetrahedron Lett., 1986, 27, 719.

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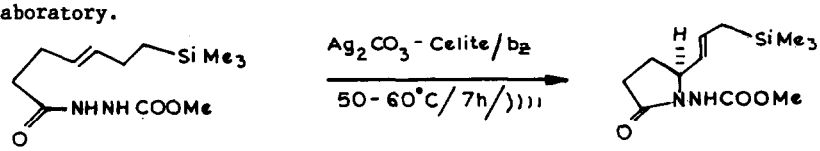
19. Further extension of the method is possible. For example, the aza-ene[24] route to 24 from the crystalline acylhydrazocarboxylate 23 (m.p. 62°C) is feasible. The utility of this protocol in the synthesis of pyrrolizidine alkaloids is under active investigation in this laboratory.



23 24

20. GC-MS of 21 reveals one major isomer (~90%) with two minor isomeric components and the side chains stereochemistry in 21 has been established to be cis from ^{1}H-NMR.

21. GC-MS of 22 reveals one major isomer (~90%) with one minor isomeric component; configuration R^1 (Me) has not been established.

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