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TWO-STEP SYNTHESIS OF ALLYLIC SILICON DERIVATIVES FROM ENONES

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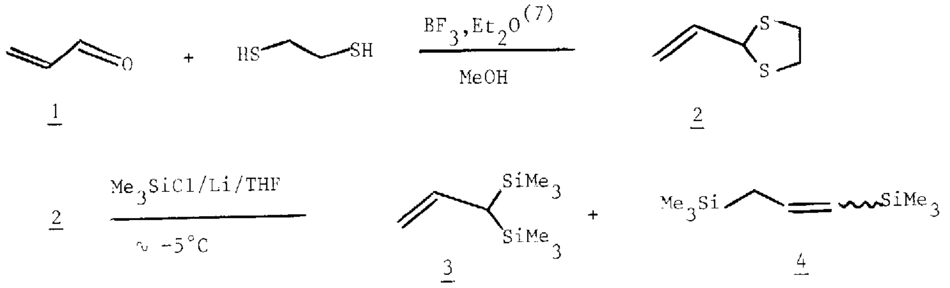
The use of allylsilanes in organic synthesis has developed quite rapidly in recent years(1)(2) and the importance of such intermediates has been established.

Since many years, we have focused our attention on this field and, for instance, synthetized β-pinenyl or Δ-1,7 p-menthenyl ketones and nitriles from terpenic allylsilanes (3)(4).

However the introduction of a trialkylsilyl group at an allylic position in relatively sensitive substrates, as are natural products, is an interesting challenge.

Reductive silylation of allylic thioethers, readily accessible from ethylenic compounds through an ene-reaction, led us easily to such allylsilanes(5). We now wish to report the synthesis of a variety of bis-silyl propenyl compounds of the type 3 and 4, starting from enones 1, through the corresponding vinylic dithiolannes 2(6), following the scheme :

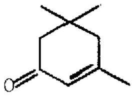
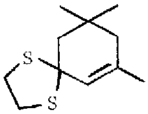
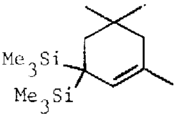
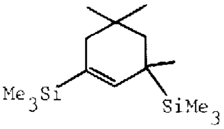
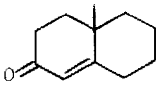
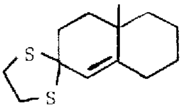
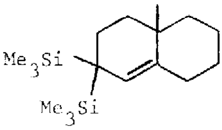
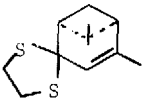
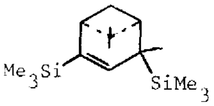
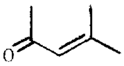
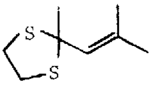
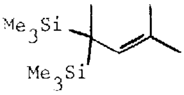
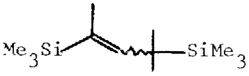
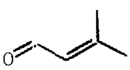
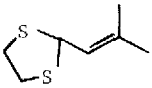
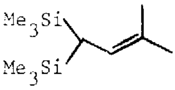
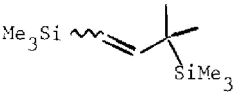
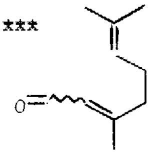
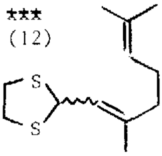
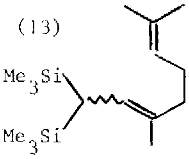
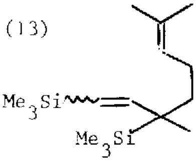
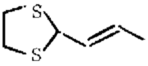
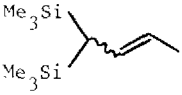
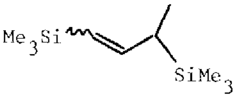


The results are summarized in the Table.

The dithiolannes 2 were always formed almost quantitatively from the enones 1, and were submitted to reductive silylation without further purification after removal of the solvent methanol.

The formation, in most cases, of a mixture of the two regio-isomers 3 and 4 is no real problem since the less stable isomer can be converted into the more stable one, for instance, on treatment with tetrabutylammonium fluoride(14). Whichever is the more stable isomer, 3 and 4 have at least one Si-C allylic bond which can be cleaved by electrophiles with allylic transposition, as examplified in the following.

-TABLE-

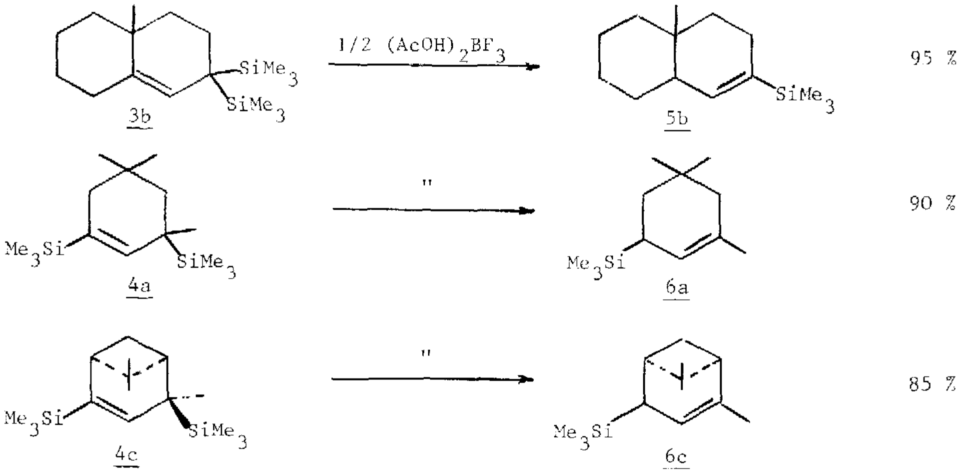
n°	1	2(8)	3(8)	4(8)	3/4	yield*
a					28/72	71 %
b	(9) 				100/0	74 %
c	(10) 			** 	0/100	76 %
d				(13) 	28/72	67 %
e	(11) 			(13) 	70/30	60 %
f	*** 	*** (12) 	(13) 	(13) 	85/15	73 %
g			(13) 	(13) 	57/43	73 %

* : *after distillation.*

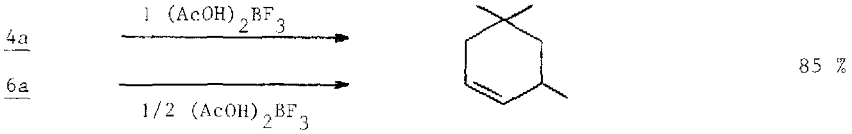
** : *one single stereoisomer is formed, most probably with a trans structure.*

*** : *mixture of Z and E isomers (1/2).*

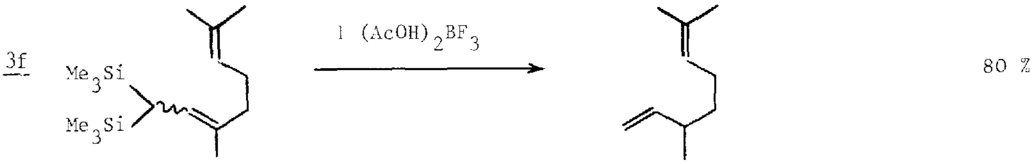
In the presence of a half-equivalent of the acetic acid/boron trifluoride complex $(AcOH)_2BF_3$ at -25°C(15), monoprotodesilylation occured, yielding either the corresponding vinylsilane 5 (from 3) or the corresponding allylsilane 6 (from 4) :



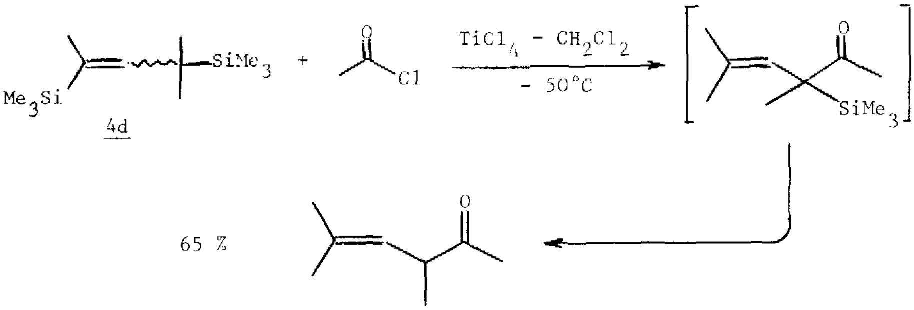
When 4a and 6a were reacted respectively with one or one half of an equivalent of this complex, 3.5.5.-trimethylcyclohexene(16) was obtained :



Similarly, 3.7-dimethyl octa 1.6-diene was obtained upon treatment of 3f with one equivalent of the complex :



We also showed that 1.3-bis-silyl propenes 4 behave, towards acylation reactions, as 3-silyl propenes, because of the lability of the remaining silyl group on the C-adjacent to the introduced carbonyl group(17). For instance :



These preliminary results demonstrate clearly that the method we propose is very suitable for the three-steps functionnalisation of terpenic skeletons.

The further development of this method and its applications to the synthesis of natural products is under current investigation in our laboratories.

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6 - The synthesis of some vinylic dithiolannes directly from enones has been reported ; see for instance :

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7 - The procedure described in reference 6b has been used.

8 - All new products present spectroscopic data (^{1}H, ^{13}C, ^{29}Si NMR and IR) entirely consistent with the assigned structure ; they have been isolated by distillation, preparative GC or HPLC, except the dithiolannes 2 which were pure enought after evaporation of the solvant.

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10 - We whish to thank P. TEISSEIRE, Scientific Director of the Société ROURE-BERTRAND-DUPONT (Grasse, France) for providing us with this sample.

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E.J. COREY and J.W. SUGGS, Tetrahedron Lett., (1975) 2647.

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