Tetrahedron Letters,Vol.22,No.47,pp 4737-4740,1981 0040-4039/81/474737-04$02.00/0
Printed in Great Britain

SYNTHESIS AND REACTIVITY OF α-LITHIO α-TRIMETHYLSILYL CYCLOPROPANES AND RELATED DERIVATIVES

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α-lithio α-trimethylsilyl cyclopropanes have been prepared by two different routes. They have been tested as precursors of alkylidene cyclopropanes, cyclopropylidienes and α-silyl α-vinyl cyclopropanes.

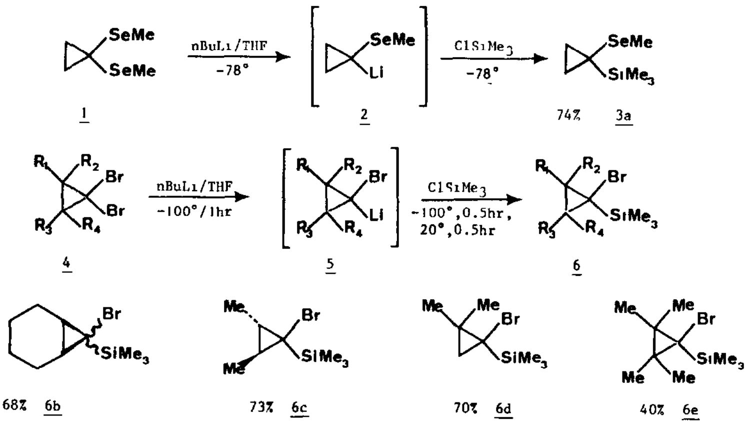
Increasing interest has been devoted the past years to the chemistry of silicon containing molecules[1]. Thus the introduction of the silyl moiety into organic compounds becomes a crucial problem.

We present in this letter our preliminary results concerning the synthesis of quite unknown α-lithio α-silyl cyclopropanes [2,3] *and their use for the synthesis of alkylidene cyclopropanes and α-silyl α-vinyl cyclopropanes.*

Whereas, α,α-dialkylsubstituted α-silyl organometallics remain still unknown [4], we have taken advantage of the well known propensity of the cyclopropyl ring to stabilize a negative charge, to prepare these first well characterized members of the series[2].

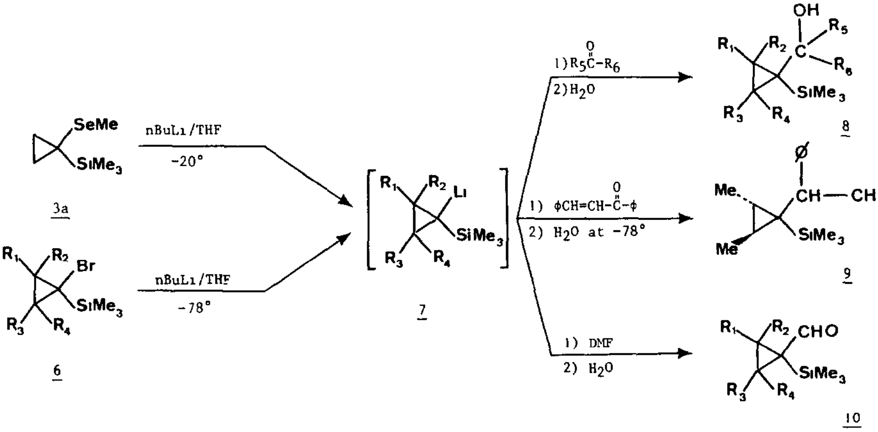
Two different routes to such compounds have been successfully tested : the selenium-metal [4,5] exchange on α-seleno α-silyl cyclopropanes 3 and the halogen-metal [2,4] exchange on α-bromo α-silyl cyclopropanes[6] 6. The required starting materials 3 and 6 have been prepared in good yield on reaction of α-lithio α-seleno cyclopropanes 2 [7] and α-lithio α-bromo cyclopropanes 5 [6] with trimethylsilyl chloride.

SCHEME I

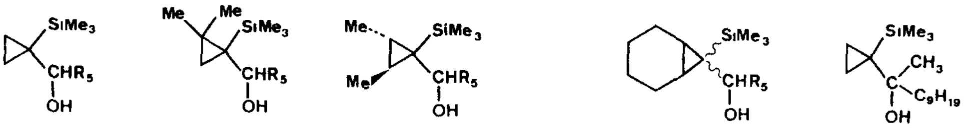


α-lithio α-silyl cyclopropanes 7 have been effectively formed on reaction of n-butyllithium with α-seleno α-silyl cyclopropane 3a (THF,-20°) and with α-bromo α-silyl cyclopropanes 6 (THF,-78°). They have been further reacted at -78° with aldehydes, ketones and N,N dimethyl formamide (Scheme II).

SCHEME II



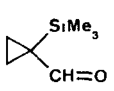
β-hydroxysilanes were isolated in moderate to good yield on reaction of 7 with undecanal (8a,8d), hexanal (8e,8i), undecanone-2 (8k) and 2-methylselenooctanal (8b,8g). They exclusively react at the C_1 site of hexenal (8c,8f,8j) and, as it is usually the case [4] at the C_3 site of chalcone thus producing the silyl ketones 9 (hydrolysis of the reaction mixture at -78°C is required to obtain the reported yield).



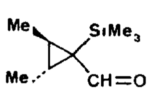
8a	R_5 $C_{10}H_{21}$	85%	8d	R_5 $C_{10}H_{21}$	71%	8g	R_5 CH(SeMe)C_6H_{13}	59%	8i	R_5 C_5H_{11}	40%	8k		40%
8b	R_5 CH(SeMe)C_6H_{13}	60%	8e	R_5 C_5H_{11}	70%	8h	R_5 CH=CH-C_3H_7	59%	8j	R_5 CH=CH-C_3H_7	10%			
8c	R_5 CH=CH-C_3H_7	72%	8f	R_5 CH=CH-C_3H_7	72%									

Interestingly the β-hydroxy γ-selenosilanes 8b and 8g quite exclusively contain the stereoisomers resulting from the attack of the organometallic on the carbonyl group as expected from the Cram or the Felkin's rules [8,9].

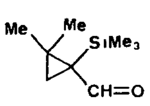
Addition of α-lithiosilanes 7a,7c,7d on an excess of DMF produces α-silyl aldehydes 10 in moderate yield and all our attempts to isolate better yield of the silyl aldehyde 10b remained unsuccessful.



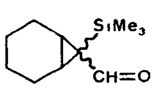
10a 80% [GC] [2]



10c 60%



10d 60%

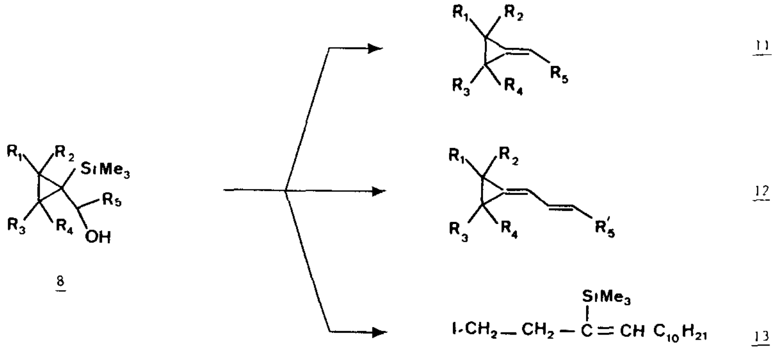


10b 10%

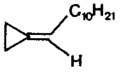
The synthesis of alkylidene cyclopropanes 11 [10] *and cyclopropylidienes 12* [11,12] *from β-hyd xysilanes 8 and of allyl silanes 14 from α-silyl aldehydes 10 or β-hydroxy γ-seleno silanes 8b was the next goal to achieve (Scheme III and IV).*

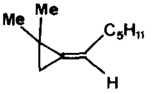
We in fact uncounter quite important difficulties for the first transformation (8 → 11). The case of olefin formation seems to be very dependent on the nature of the β-hydroxysilane and the conditions used. For example, the β-hydroxysilane 8a is recovered unchanged on reaction with KH (THF,20°,20hr)[1] or (THF,60°,12hr) even if the reaction is conducted in the presence of HMPT (THF,HMPT,1eq.,60°,15hr). 1-Iodo-3-trimethylsilyl-3-tetradecene 13 is produced in 73% yield on reaction of 8a with PI_3 (NEt_3/CH_2Cl_2/0°C/0.5hr) (Scheme III) and finally the desired alkylidene cyclopropane 11a is formed in 46% yield on reaction with $SOCl_2/NEt_3$ in CH_2Cl_2 at 0°C followed by reaction of the resulting crude product with tetra-n-butyl ammonium fluoride in DMSO (20°,15hr)[1,13]. Similarly KH/THF at 20° does not produce an alkylidene cyclopropane from 8e (24hrs) but 11i (2.5hr;100%) and 11k (60hr,88%) are formed in high yields from the corresponding β-hydroxysilanes under similar conditions.

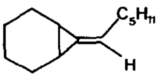
SCHEME III

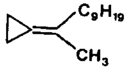


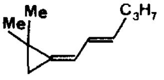
The synthesis of cyclopropylidienes 12 from the corresponding β-hydroxysilanes 8 proved to be more easy and more reliable, for instance 12f and 12h have been prepared in 76% and 71% yield on reaction of 8f and 8h with KH/THF at 20° (for 1hr and 20hr respectively). *Scope and limitations of these Peterson olefination reactions are still studied in our laboratory.*

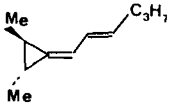










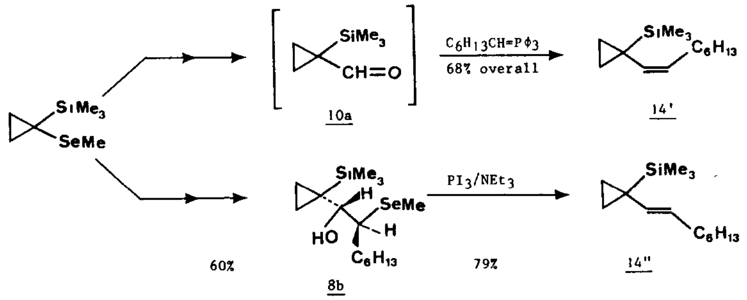


KH/THF	11a (0%)	11e (0%)	11i (100%)	11k (88%)	12f (76%)	12h (71%)
$SOCl_2$ then $R_4\overset{+}{N}F^-$	11a (46%)					

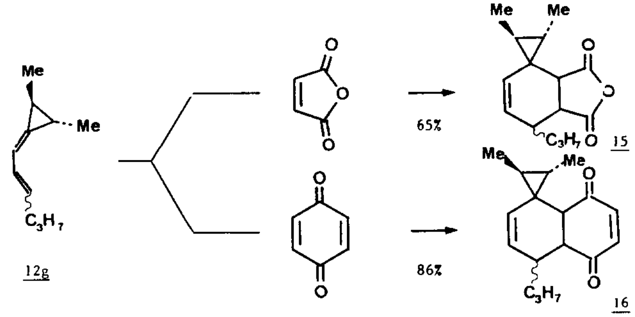
On the other hand, allylsilanes 14 have been prepared on reaction of the crude solution of silyl aldehyde 10a with n-heptylidene triphenylphosphorane (generated from the corresponding phosphonium salt and nBuLi in THF) and on reaction of the β-hydroxyselenide 8b with PI_3 (PI_3, 1eq. NEt_3/CH_2Cl_2, 0°, 0.5hr). The two allylsilanes of different origins proved to be different by |GC|[2] and NMR. The Z and E stereochemistry was respectively assigned to 14' and 14" (see scheme) on the basis of their spectroscopical data and in relation with our previous work on 1-heterosubstituted 1-vinyl 1-cyclopropanes[9].

The authors are grateful to I.R.S.I.A. (Belgium) for a fellowship to S.H. and to F.N.R.S. (Belgium) for financial support.

SCHEME IV



Finally, we have reacted the diene 12g with maleic anhydride and p-benzoquinone. The Diels-Alder reaction [12] proceeds smoothly in the two cases (benzene/20°/20hr) producing the cyclohexenes 15 and 16 in good yield. We are currently investigating the stereochemistry of these adducts



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(Received in UK 31 July 1981)