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SILICON IN ORGANIC SYNTHESIS. 14. FIVE RING ANNULATION PROCESSES BASED UPON THERMAL REARRANGEMENT OF (1-TRIMETHYLSILYLCYCLOPROPYL)ETHYLENES[1]

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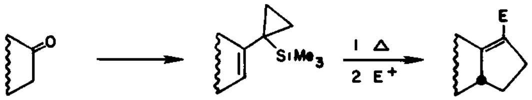
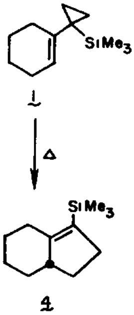
Summary Pyrolysis of (1-trimethylsilylcyclopropyl)ethylenes affords silyl substituted cyclopentenes in high yield. Subsequent reaction of these products with varied electrophiles forms the basis of a new and versatile five-ring annulation sequence.

The vinylcyclopropane rearrangement, first discovered in the late 1950's,[3] immediately became the subject of intense mechanistic investigation.[4] In more recent years, the synthetic value of this reaction has gained substantial attention, especially in terms of its usefulness as a cyclopentane annulation scheme.[5] In the preceding paper,[1] the preparation of (1-trimethylsilylcyclopropyl)ethylenes was described, and the reluctance of these molecules to undergo acid-catalyzed ring expansion detailed. Herein we disclose that such functionalized vinylcyclopropanes can be smoothly rearranged under thermal conditions. Since the resulting vinylsilanes are subject in turn to electrophilic substitution,[6] these conversions constitute a new five-ring annulation procedure of rich diversity, as represented by



Passage of 1-3 in the gas phase at 30-40 torr (nitrogen as carrier gas) through a quartz chip-packed tube (30 cm long) heated to 570°C (flow rate 6 ml/min) gave 4 (80%), 5 (82%), and 6 (71%), respectively.[7] As expected, the Z isomer of 3 did not give 6 under these conditions due to steric inhibition by the cis-oriented methyl group.[8] Incorporation of the double bond into a cyclic enone



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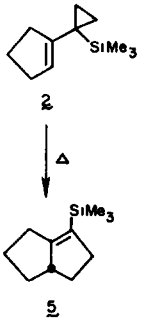

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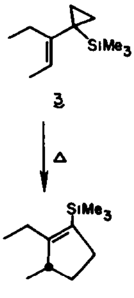

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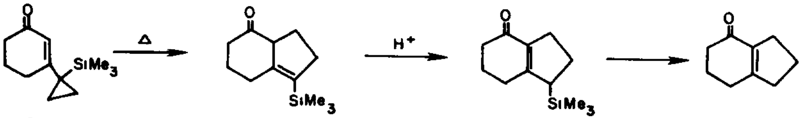
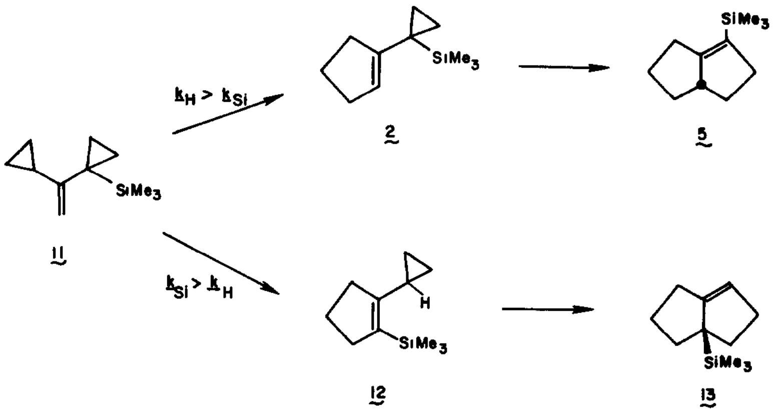


7 8 9 10

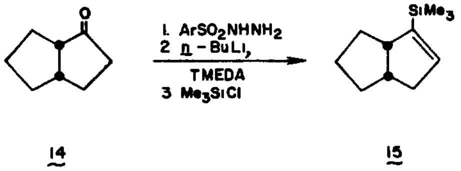
moiety as in 7[8] did not disrupt the bond relocation process, although somewhat more elevated temperatures (660°C) were now required. Compound 8 (75% yield) is particularly prone to prototropic shift and formation of 9. Because the trimethylsilyl group in 9 is allylic, desilylation to give 10 occurs readily during the chromatographic purification process.

If the thermolyses described herein proceed by a stepwise pathway, the silicon-bearing carbon must acquire odd-electron character in the intermediate biradical. Since α-silyl free radicals are known to lack stabilization,[10] the -SiMe$_3$ group should exert an untoward effect in 1-3 and related compounds. Although the somewhat elevated temperatures required can be construed to be an indication of rate retardation, we sought to acquire additional evidence. Although kinetic studies of vinylcyclopropane rearrangements abound,[11] no intramolecular competition version of this process has been documented. Although quantitative information is not usually derivable from experiments of this type, a qualitative appreciation of kinetic ordering can be gained with certainty, frequently with minimal expenditure of effort. For these reason, we prepared the dicyclopropylethylene 11.[12]

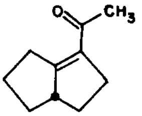
As the scheme indicates, kinetically favored involvement of the unsubstituted three-membered ring will lead initially to 2 and ultimately to 5. To the extent that the silicon substituted cyclopropane enters first into isomerization, vinylsilane 12 will result. Should 12 be labile to the thermal conditions, allylsilane 13 will be produced. Experimentally, pyrolysis of 11 under the predescribed conditions resulted in clean conversion uniquely to 5 (80%). We conclude therefore that $k_H \gg k_{Si}$.



A particularly attractive feature of the present procedure is the fact that the mono- and bicyclic vinylsilanes which are formed invariably have their double bond positioned in the more highly substituted site. This regiochemistry is not attainable through application of the Shapiro reaction which leads via kinetically controlled proton abstraction to the lesser substituted vinylsilane[13] (e.g., 14 → 15). As a result, the methodologies are usefully complementary.



In vinylsilanes, the silicon atom generally directs entry of the electrophile to the silicon-bonded carbon atom in order to take advantage of the substantial cationic stabilization which can be provided by the adjacent C-Si sigma bond. We have observed that vinylsilanes such as 4-6 likewise conform to the pattern of regioselectivity. However, conditions must be more strictly controlled than normal, perhaps as a consequence of the tetrasubstituted nature of their double bonds. Thus, 2 and 3 are transformed into 16 and 17, respectively, upon exposure to acetyl chloride and $AlCl_3$ in CH_2Cl_2 at -78°C (1.5 hr). In like fashion, the bromination of 5 (CH_2Cl_2, -78°C → 20°C, 30 min) leads to 18.



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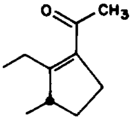

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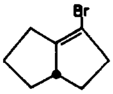

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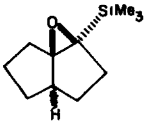
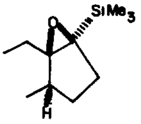


19a, β-H
b, α-H



20a, β-H
b, α-H

These substrates also serve as starting points for the generation of epoxysilanes which, although highly reactive, are capable of purification with isomer separation. Through reaction with m-chloroperbenzoic acid in CH_2Cl_2 at 0°C (30 min), 5 was efficiently transformed into a 60 40 mixture of the epimers of 19 (the individual stereochemistries of these isomers was not revealed by lanthanide shifting experiments). In the case of 6, a 1 1 mixture of 20a and 20b was isolated. The established chemical versatility of epoxysilanes[6,14] suggests that 19 and 20 might have considerable synthetic potential in their own right. This facet of the methodology has yet to be explored.[15]

References and Notes

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(2) National Institutes of Health Postdoctoral Fellow, 1980-1981.

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(7) All new compounds described herein gave correct elemental analyses and spectral data (^1H NMR, IR, m/e) in accord with the assigned structures.

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(9) Enone 7 was prepared in two steps (80% overall yield) by condensation of 3-methoxy-2-cyclohexen-1-one with α-trimethylsilylvinyllithium, followed by Simmons-Smith cyclopropanation. Alternatively, a 91% yield of 7 could be achieved by direct condensation with 1-lithio-1-trimethylsilylcyclopropane.[1]

(10) For example Sommer, L.H., Dorfman, E., Goldberg, G.M., Whitmore, F.G. J. Am. Chem. Soc. 1946, 68, 488.

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(12) The synthesis of 11 began with acetaldehyde and involved the following steps (a) $CH_2{=}C(Li)SiMe_3$, ether, -78°C; H_2O, (b) C_2H_5ZnI, CH_2I_2, ether, reflux 10 hr, NH_4Cl, H_2O, (c) PCC, NaOAc, CH_2Cl_2, 25°C, (d) cyclo-C_3H_5Li, ether, 25°C, NH_4Cl, H_2O, (e) $(C_2H_5)_3\overset{+}{N}{-}SO_2{-}\overset{-}{N}{-}CO_2CH_3$, C_6H_6, reflux, 7 hr.

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