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1-HYDROXYCYCLOPROPANECARBOXALDEHYDE TETRAHYDROPYRANYL ETHER. PREPARATION AND REARRANGEMENT OF FUNCTIONALIZED 1-VINYLCYCLOPROPANOLS.

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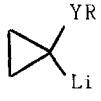
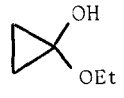
SUMMARY : The tetrahydropyranyl ether of 1-hydroxycyclopropanecarboxaldehyde, readily available from 1-hydroxycyclopropanecarboxylic acid, allows the preparation of functionalized 1-vinylcyclopropanols which undergo specific four- or five-membered ring annulations.

Cyclopropanes have recently gained substantial attention especially in terms of their usefulness as building blocks for molecular construction involving the release of strain energy to provide the driving force for carbon framework rearrangement.



1a YR = SAr c = $SeCH_3$, SePh
b = OCH_3 d = $Si(CH_3)_3$



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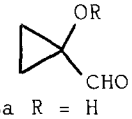
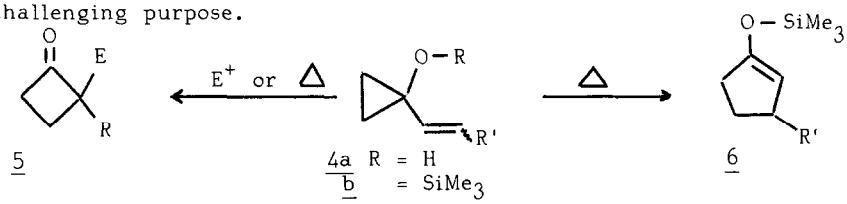


3a R = H
b = THP

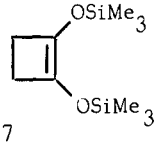
Thus for instance, besides 1-lithiocyclopropyl arylsulfides 1a (1), methylether 1b (2), alkyl/aryl selenides 1c (3) and trimethylsilane 1d (4) which have been recently used to get four and five ring annulations, the cyclopropanone ethyl hemiacetal 2 (5) and the 1-hydroxycyclopropanecarboxaldehyde derivative 3b (6), which provide readily 1-vinylcyclopropanols (6,7,9), appear to be also participant of choice for this challenging purpose.



5 4a R = H
b = $SiMe_3$ 6

As a matter of fact, cyclopropanols 4a undergo $C_3 \longrightarrow C_4$ ring expansion into cyclobutanone derivatives 5 either by addition of electrophilic reagents (HBr, pTsOH, conc. sulfuric acid, Cl^+, OH^+ ....) (9) or on heating at around 100°C (10) ; while, silylated cyclopropanols 4b undergo thermal $C_3 \longrightarrow C_5$ ring enlargement into the silyl enol ether of cyclopentanone derivatives 6 (1,7,8) which then can be regiospecifically alkylated to give 2,3-disubstituted cyclopentanones (7) or cyclopentenones (6).

In the course of studies designed to develop the unique advantage offered by this class of reagents in synthesis we report a convenient synthesis of the tetrahydropyranyl ether of the 1-hydroxycyclopropanecarboxaldehyde 3b and from this new synthon the preparation of some functionalized 1-vinylcyclopropanol derivatives which undergo specific ring expansion to provide readily valued synthetic compounds (see also the accompanying paper).



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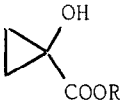
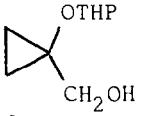


8a R = CH_3
b = H



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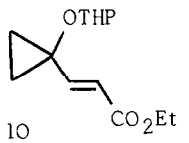
Although the 1-hydroxycyclopropanecarboxaldehyde 3a cannot be isolated because it undergoes unavoidable ring expansion into 2-hydroxycyclobutanone (11) ; on the other hand, its tetrahydropyranyl ether 3b is stable enough to be handled. It can be either prepared, as we have recently reported, from the methyl 1-hydroxycyclopanecarboxylate 8a (6), product of methoxide ion induced ring contraction of the labile 1,2-cyclobutanedione (12) ; or more conveniently, 3b can be prepared from the 1-hydroxycyclopropanecarboxylic acide 8b obtained after successive addition of bromine and iced-water (13) to the readily available 1,2-disiloxycyclobutene 7 (14). Then, esterification by methanol and thionyl chloride (15) gave the ester 8a in 98.5% yield ; tetrahydropyranylation (16) and lithiumaluminum hydride reduction led to the cyclopropylcarbinol 9. Finally, oxidation with oxalyl chloride activated dimethylsulfoxide (17) provided the expected aldehyde 3b in 88% overall yield from 8b.



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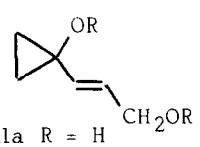
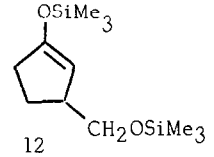


11a R = H
b = $SiMe_3$



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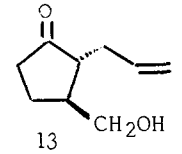

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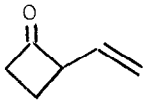
Addition of triethylphosphoacetate carbanion in THF to aldehyde 3b gave the trans vinylcyclopropane 10 (18) in 88% yield ; reduction of the ester 10 with DIBAH to minimize conjugate reduction, deprotection of the THP group by action of pyridinium p-toluenesulfonate (PPTS) in ethanol at 55°C (16) led to the diol 11a. Double silylation by action of trimethylsilylchloride and triethylamine in the presence of a catalytic amount (5 mol %) of dimethylsulfoxide (7,19) gave the trans disiloxyvinylcyclopropane 11b in 80% overall yield from 10. On flash thermolysis at 600°C, 11b underwent $C_3 \rightarrow C_5$ ring enlargement into the regiospecific silylated cyclopentanone enol ether 12 which, upon treatment with methyllithium (2 equiv.) to generate the lithium enolate (20) followed by the addition of allyl bromide in 1,2-dimethoxy-ethane at -20°C led, in 62% yield to the trans 2-allyl 3-hydroxymethylcyclopentanone 13. It must be underlined that the acetal of 13 has been previously used as precursor of the ($\pm$) 11-deoxyprosta-

glandin E_2 methyl ester (21,22). So, the sequence 3b ⟶ 13 provides a convenient route to this useful synthon.



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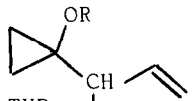
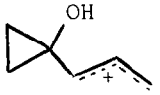


15a R = THP
b = H



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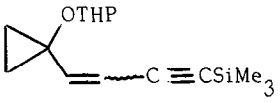
On the other hand, upon addition at room temperature of a catalytic amount of boron trifluoride ethyl etherate, the diol 11a underwent total dehydration and ring enlargement into the 2-vinylcyclobutanone 14 (23). Furthermore, addition of vinylmagnesium bromide to the aldehyde 3b provided the vinyl alcohol 15a and after removal of the THP group (16), the 1-(1-vinylcarbinol) cyclopropanol 15b. Upon addition of a catalytic amount of BF_3 , Et_2O the diol 15b underwent also dehydration and ring expansion into 14, within 15 mn at room temperature as monitored by TLC. Likely, the rearrangement of both vinylogous diols 11a and 15b involves the intermediate formation of the same cyclopropylcarbinyl cation 16 (24).



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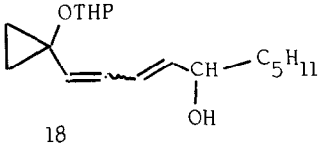

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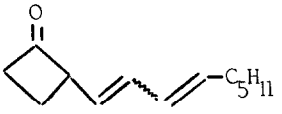

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Peterson olefination of the aldehyde 3b with 1-trimethylsilylpropyn-3 yllithium (25), furnished the Z,E mixture of enynes 17 in 85% yield. Desilylation of 17 by means of potassium fluoride in DMF (26), metalation with n-butyllithium, condensation with hexanal and lithiumaluminum hydride reduction gave the conjugated dienol 18 in 92% yield. Then treatment of 18 by (10 ml. %) PPTS (16) in ethanol in order to remove the THP group led directly to the 2 (1,3-nonadienyl)-cyclobutanone 19 (27), within 30 min. at 55°C as monitored by TLC. So, this $C_3 \longrightarrow C_4$ ring enlargement occurs in rather mild acidic conditions (pH of a M aqueous solution of PPTS is 3.0 (16)). 2-Vinylcyclobutanones, which are useful intermediates for the elaboration of 5- and 6- (2) or 8-membered rings (28,29) have been recently obtained from the fluoboric acid induced ring enlargement of 1-arylthio (24) and 1-methoxycyclopropylcarbinols (2) prepared from the lithiocyclopropane derivatives 1a and 1b, respectively. The high propensity of vinylcyclopropanol derivatives such as 11a, 15b and 18 to undergo $C_3 \longrightarrow C_4$ ring expansion provides a convenient alternate pathway to such elaborate compounds. (For other examples of ring expansion of vinylcyclopropanols, see the accompanying paper).

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