Ring Contraction of 2-Alkylidenecyclobutanols to Cyclopropyl Carbonyl Compounds

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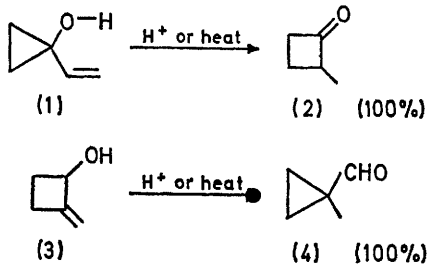
Summary 2-Alkylidenecyclobutanols when heated in a sealed tube or in 5% H_2SO_4 undergo ring contraction to 1-alkylcyclopropyl carbonyl compounds; subsequent rearrangement into homoallylic carbonyl derivatives occurs when 1,5 hydrogen transfer is possible.

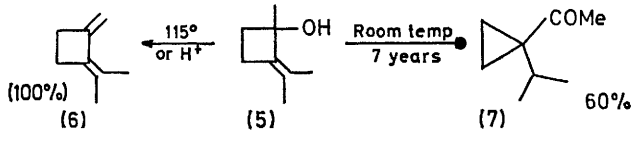
1-VINYLCYCLOPROPANOLS (**1**) readily undergo ring expansion into cyclobutanone derivatives (**2**) by addition of electrophilic reagents[1] or on heating (*ca.* 100°).[2] The stereospecificity of this rearrangement and its preparative value have been discussed.[2]

We report that the 2-alkylidenecyclobutanols (**3**) undergo a similar acidic or thermal ring contraction to 1-alkyl cyclopropyl carbonyl compounds (**4**). The conditions required for this ring contraction are more vigorous, however, and in certain cases other rearrangements occur.

2-Methylenecyclobutanol (**3**) was readily prepared from 2-hydroxycyclobutanone[3] by Wittig treatment of the tetrahydropyranyl ether derivative, followed by rapid acidic hydrolysis at room temperature. On heating in a sealed tube at 245° for 4 h or on treatment with 5% H_2SO_4 at 100° for 30 min, (**3**) is quantitatively converted into 1-methylcyclopropanecarbaldehyde (**4**). The ring contraction of (**3**) can be readily followed by n.m.r.

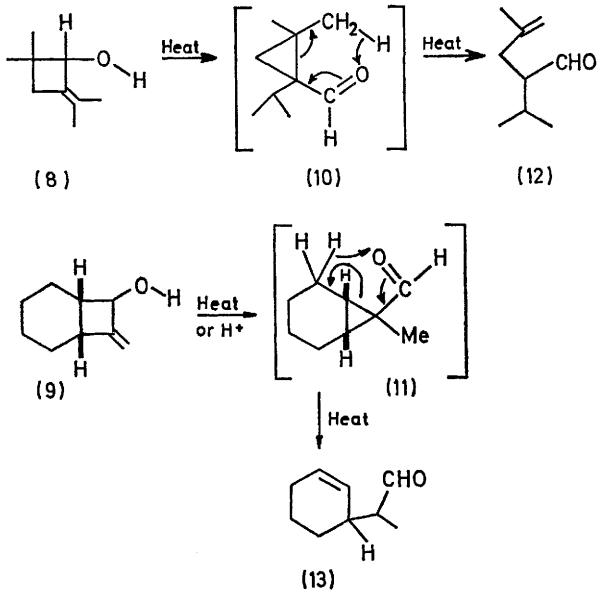


The ring contraction appears to be general and has contributed to our understanding of other reactions. For example, the cyclobutanol (**5**) undergoes dehydration on heating to form (**6**). A sample of (**5**) kept in a sealed tube



at room temperature for 7 years has been found to undergo ring contraction to give the cyclopropyl ketone derivative (**7**).†

In the same way, the cyclobutanols (**8**) and (**9**)‡ undergo thermal ring contraction. But, under the conditions used (245°, 4 h), the aldehydes (**10**) and (**11**), having a γ hydrogen readily undergo ring opening[4] forming the homoallylic aldehydes (**12**) and (**13**), respectively,† and the cyclopropyl carbonyl compounds (**10**) and (**11**) cannot be isolated.



However, the ring contraction of (**9**) in acidic medium (5% aq. H_2SO_4, 100°) can be followed by n.m.r. which shows the formation of the intermediate (**11**) which then rearranges to (**13**) on further heating. As we know that the ring contraction of the cyclobutanol (**3**) leads to the same product (**4**), on heating or under acidic conditions, it follows that (**10**) and (**11**) can be assumed to be intermediates in the thermal rearrangement.

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† Structural assignments are based on i.r., n.m.r., and m.s. evidence.

‡ The synthesis of these cyclobutanols will be reported in the full paper.

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