Thermally Induced Retro-Claisen Rearrangement of Formyl-ethynyl-cyclopropanes

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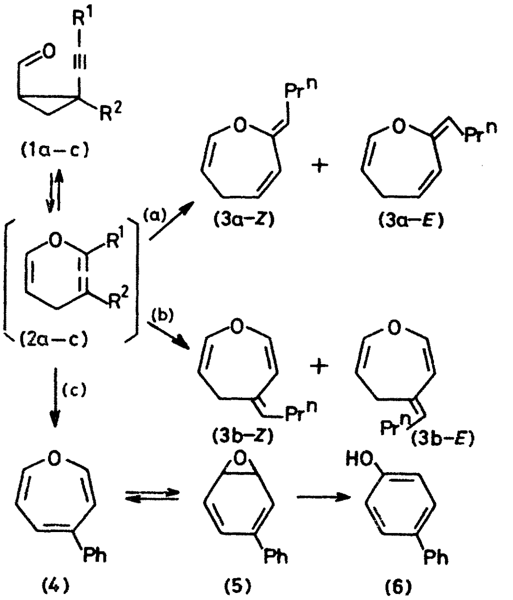
Summary The retro-Claisen rearrangement of the formyl-ethynyl-cyclopropanes (**1a–c**) followed by a [1,3] hydrogen shift yields two types of products depending on the nature and position of the substituents: the alkylidene-dihydro-oxepins (**3a–c**) and the phenol (**6**).

Few examples of retro-Claisen rearrangements of $\gamma\delta$-ethylenic carbonyl derivatives to allyl vinyl ethers are known. An equilibrium is generally observed[1] unless the resulting ether is stabilized by conjugation[2] or possesses lower steric strain than the carbonyl compound.[3] Participation of an acetylenic bond has never been observed.

We recently reported[4] our study of the valence isomerization of *cis*-2-alkynyl-3-vinyl-oxirans to *cis*-1-formyl-2-alkynyl-cyclopropanes (**1**) in the gas phase. We have now examined the thermal behaviour of (**1a–c**) in sealed tubes (CCl_4 solutions, 130—150 °C). The cyclopropanes (**1a**) and (**1b**) were converted into the seven-membered heterocycles (**3a**) (30% yield after 1·5 h at 132 °C, 40% yield after 2·5 h at 132 °C; *Z/E ca.* = 3) and (**3b**) (90% yield after 1 h at 150° C; *Z/E ca.* = 1), respectively, whereas (**1c**) gave rise quantitatively to the phenol (**6**)† (>90% yield after 1 h at 130 °C).

The structures of (**3a**) and (**3b**) have been assigned by ^1H n.m.r. spectroscopy. The chemical shifts and coupling constants are closely related to those reported for 4,5-dihydro-oxepin[5] and 2,5-dihydro-oxepin.[1b] The *Z* and *E* isomers were separated by column chromatography and the configurations of the *exo* double bonds were assigned by comparison with the chemical shifts of similar diene[6] and enol ether systems.[7]‡



a; R^1 = Bu^n, R^2 = H
b; R^1 = H, R^2 = Bu^n
c; R^1 = H, R^2 = Ph

The thermolytic behaviour of the compounds (**1**) seems to be governed by a retro-Claisen rearrangement involving the triple bond, to give, in a first reversible step, the strained oxacycloheptatrienes (**2a–c**); such intermediates

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† M.p. and ^1H n.m.r. spectral data were identical to published data for this commercial compound.

‡ Satisfactory analytical results were obtained for all new compounds. Spectral data will be published elsewhere.

have already been postulated for the thermal isomerization of a vinyl-ethynyl-cyclopropane[8] or -oxiran.[4] In a second step, this cyclic allene undergoes a [1,3] hydrogen shift leading to (**3a**), (**3b**), or (**4**). It appears from the products isolated that formation of an exocyclic double bond is favoured since the endocyclic migration only takes place for (**2c**). The oxepin (**4**), which is in equilibrium[9] with the arene oxide (**5**), cannot be isolated, but is converted under these conditions into the phenol (**6**), in agreement with the well documented thermal instability of these compounds.[10]

Some aspects of the mechanism are not yet clear. Compound (**1a**) did not isomerize in the gas phase at these temperatures; we therefore suggest that (**1**) and (**2**) exist in a tautomeric valence equilibrium, the cyclopropane form being highly favoured in the gas phase, whereas, in the liquid phase, a catalytic hydrogen transfer shifts this equilibrium.

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