A Novel Thermal Rearrangement of a Propargyl Vinyl Alcohol

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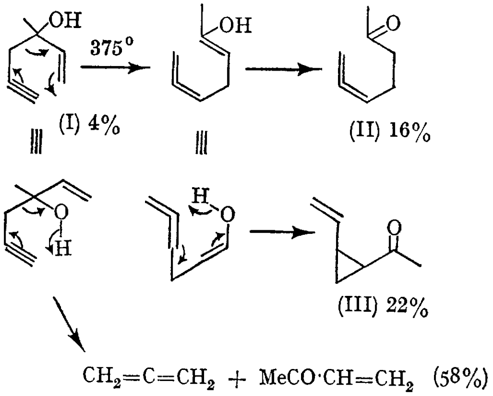
SEVERAL groups have recently reported thermal rearrangements of acetylenic compounds.[1] We have dealt with a propargyl vinyl system which provides, in addition to the expected allenic product, the product of an unusual closure to a three-membered ring. When 3-methylhex-1-en-5-yn-3-ol is carried in nitrogen through a vertical Vycor tube packed with Berl saddles and heated to 375°, four products are formed. They are, in addition to unchanged starting material, hepta-5,6-dien-2-one (II), 1-acetyl-2-vinylcyclopropane (III), methyl vinyl ketone, and allene. The percentages by each formula represent approximate mole percentages of the residue remaining after the allene had evaporated into a separate trap. They were determined by vapour phase chromatography. If it is assumed that the molar amount of allene equalled the molar amount of methyl vinyl ketone, then all the pyrolysed starting material is accounted for in these products. They were separated by preparative scale v.p.c. The allenic ketone (II) was identified by i.r. and n.m.r. spectra and by the observation that two equivalents of hydrogen were taken up to form heptan-2-one. The cyclopropyl compound (III) was identified by i.r. and n.m.r. spectra as well as by comparison with material prepared by the treatment of the acid chloride of 2-vinyl-1-cyclopropanecarboxylic acid[2] with dimethylcadmium. The v.p.c. retention time and i.r. spectrum of the synthetic material were identical to those of the thermal product. The n.m.r. spectra of the two samples were closely similar. Preliminary analysis of the 100 MHz. n.m.r. spectrum indicates that the thermally-produced material is the *trans*-isomer. Compound (III) also takes up hydrogen to form heptan-2-one.

The formation of the four products is rationalized by the several concerted electronic reorganizations shown. Compound (II), an acetylenic analogue of the product of an "oxy-Cope" rearrangement,[3,4] was the expected product and is similar to the allenic products obtained by Landor[1a] and Huntsman.[1b] Compound (III) may be formed in a rearrangement which finds precedent in the "enolene" rearrangements of Roberts and his co-workers.[5] These authors provide evidence for the transient formation of acyl alkyl cyclopropanes during the thermal rearrangement of $\gamma\delta$-unsaturated ketones. Hydrogen transfers from the methyl-carbon instead of the hydroxyl group are not excluded by the present evidence. Concerted mechanisms for the formation of (II) and (III) are assumed but not proved. Allene and methyl vinyl ketone undoubtedly are formed by a concerted mechanism, for had cleavage to two radicals occurred, the propargyl radical would have abstracted a hydrogen atom to form propyne rather than allene.[4,6]



(I) 4%

(II) 16%

(III) 22%

$CH_2{=}C{=}CH_2 + MeCO{\cdot}CH{=}CH_2$ (58%)

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