A Novel Steric Effect in the Thermolysis of Prop-2-ynylvinyl-carbinols[1]

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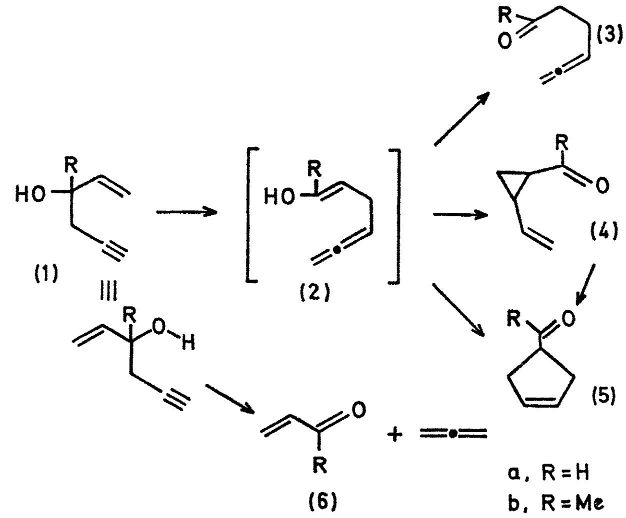
Summary The formation of both acetylvinylcyclopropane and 4-acetylcyclopentene during the thermolysis of 3-methylhex-1-en-5-yn-3-ol has been verified and the mechanistic discontinuity can be interpreted on the basis of a torsional effect in the transition state.

AMONG the increasing number of electrocyclic reactions involving acetylenic bonds which have been reported recently, are three thermolyses of prop-2-ynylvinyl-carbinols with anomalous results. All three reports agree on the formation of (**3**), the acetylenic oxy-Cope product[2] and of (**6**), and allene, the products of β-hydroxy-olefin cleavage. There is disagreement, however, about the formation of (**4**) or of (**5**). Thus, we have found[2] thermolysis of (**1a**) to yield (**5a**) as the only cyclized product, in agreement with Chuche and Manisse who have reported[3] (**1b**) to form only (**5b**). Wilson and Sherrod, however, reported[4] (**1b**) to produce only (**4b**). The picture is further complicated by the recent suggestion that the transformation of (**4**) to (**5**) may be considerably easier than earlier reports had indicated.[5]



Product distribution in thermolysis of (**1b**)

Temp. (°)	Press. (mm)	Product formation (%) Cleavage	Product formation (%) Rearrangement	Composition of Rearranged fraction (%) (3)	(4)	(5)
330	1	31	69	61	39	0
	22	29	71	56	32	11
350	1	32	68	59	31	10
	22	33	67	44	27	29
380	1	38	62	53	15	32
	22	37	63	39	9	52

The thermolytic behaviour of (**1b**) has therefore been re-investigated over a wider range of experimental conditions than were utilized in either of the conflicting reports. Both cyclic products, (**4b**) and (**5b**), could be produced in the flow apparatus described previously.[6] The data, summarized in the Table, confirm that the ratio of cleavage to rearrangement products is independent of residence time in the heated zone (*i.e.*, varying pressure); the distribution of the various rearrangement products, however, is not. The decrease of (**3**) with increasing temperature and with increasing residence time is indicative of the formation of (**3**) from its enolic precursor as has been noted.[2] The pressure dependence of the ratio of (**4b**) : (**5b**) implies that direct conversion of (**2b**) into (**5b**) is not the only pathway for the formation of (**5b**). Consequently, when a sample of pure (**4b**) was thermolysed at 380° and 22 mm, the product was found to consist of (**5b**) and unreacted (**4b**) in a 7 : 1 ratio. A modified Arrhenius plot, however, indicates that the amount of (**5b**) produced during thermolysis of (**1b**) is in excess of the amount which could have formed through the intermediacy of (**4b**) alone.†

The 100 MHz n.m.r. spectrum of (**4b**) indicates the compound to be largely in the *trans*-form, with a minor *cis*-constituent.‡ The survival of some (**4b**) under the rigorous conditions used to demonstrate its direct conversion into (**5b**) indicates an activation energy substantially higher than that implied[5] for the transformation of *cis*-(**4a**) to (**5a**) and suggests a biradical pathway analogous to the formation of 4-methylcyclopentene from *trans*-methylvinylcyclopropane.[7] No dihydro-oxepins were detected in any of the products of thermolysis of (**1a**) or (**1b**), in accord with the absence of any substantial amounts of *cis*-(**4**).[5]

Both previous reports[3,4] represent extreme experimental conditions. At 370—430° and 30 mm, as utilized by Chuche and Manisse, no (**4b**) survives. Wilson and Sherrod, on the other hand, although operating at 375°, appeared to use an exceedingly short residence time (*i.e.*, the only report where starting material survives) and thus were only able to detect (**4b**).

The data indicate that the process (**2b**) → (**5b**) is a higher energy process than (**2b**) → (**4b**). However, in the absence of the 3-methyl substituent no cyclopropane derivative can be detected.[2] The subtle steric influence of the methyl group, far removed from the reaction site, becomes apparent upon consideration of the requisite transition states, (**7**) and (**8**), for the two intramolecular cyclizations. The transfer of the hydroxyl proton to the central atom of

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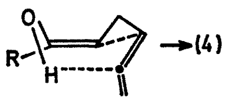
† See footnote 20 in ref. 2 for the appropriate equation. The marked deviation from linearity lies in the direction of a contribution to the total amount of (**4b**) + (**5b**) by a direct (**2b**) → (**5b**) pathway.

‡ We thank Professor R. Stolow for obtaining this spectrum.

the allene[2] requires a *cis*-configuration of the enol. The structure of the product then depends upon the choice of C-2–C-4 *versus* C-2–C-6 bond formation. During this process, a slight twist of the enolic double bond seems inevitable before re-hybridization to *sp*^{3} at C-2 is completed. The consequence is seen in the corresponding projections, taken along the C-1–C-2 bond axis. With R = Me, additional energy is required, due to eclipsing with the adjoining proton, for the formation of (**5b**) and the alternate pathway, *via* (**7**), leading to (**4b**) can now compete successfully. With R = H, this effect is smaller, the more strained state (**7a**) cannot compete and only (**5a**) is detected. This interpretation has some precedence in the torsional effect invoked by Schleyer in the norbornanes.[8]



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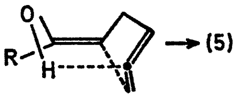

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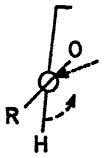

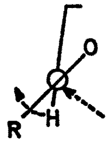

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