

A Novel Steric Effect in the Thermolysis of Prop-2-ynylvinyl-carbinols¹

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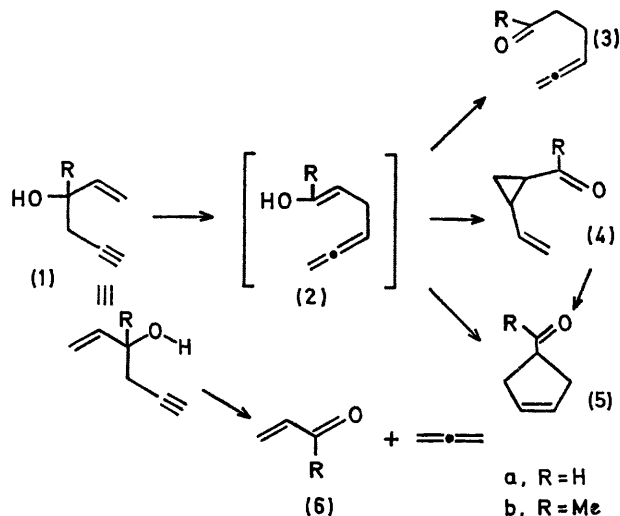
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Summary The formation of both acetylvinylcyclopropane and 4-acetylcyclopentene during the thermolysis of 3-methylhex-1-en-5-yn-3-ol has been verified and the mechanistic discontinuity can be interpreted on the basis of a torsional effect in the transition 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 product² 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 found² thermolysis of (1a) to yield (5a) as the only cyclized product, in agreement with Chuche and Manisse who have reported³ (1b) to form only (5b). Wilson and Sherrod, however, reported⁴ (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

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

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 implied⁶ 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



Product distribution in thermolysis of (1b)

Temp. (°)	Press. (mm)	Product formation (%)		Composition of Rearranged fraction (%)		
		Cleavage	Rearrangement	(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

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

of the products of thermolysis of (1a) or (1b), in accord with the absence of any substantial amounts of *cis*-(4).⁵

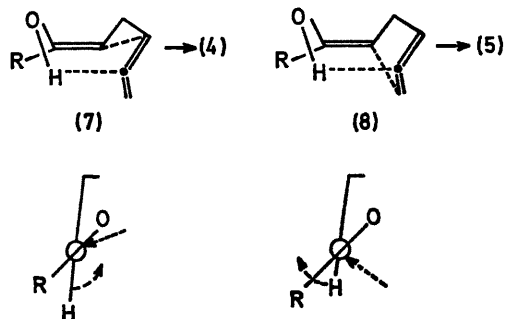
Both previous reports^{3,4} represent extreme experimental conditions. At 370–430° and 30 mm, as utilized by Chuche and Manisse, no (4b) survives. Wilson and Sherrod, on the other hand, although operating at 375°, appeared to use an exceedingly short residence time (*i.e.*, the only report where starting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

[†] 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 allene² 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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¹ For previous paper, see A. Viola and E. J. Iorio, *J. Org. Chem.*, in the press.

² A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, 1968, **90**, 6141.

³ J. Chucho and N. Manisse, *Compt. rend.*, 1968, **267**, C, 78.

⁴ J. W. Wilson and S. A. Sherrod, *Chem. Comm.*, 1968, 143.

⁵ S. J. Rhoads and R. D. Cockroft, *J. Amer. Chem. Soc.*, 1969, **91**, 2815.

⁶ A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *J. Amer. Chem. Soc.*, 1967, **89**, 3462.

⁷ W. R. Roth and J. König, *Annalen*, 1965, **688**, 28.

⁸ P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 701.