

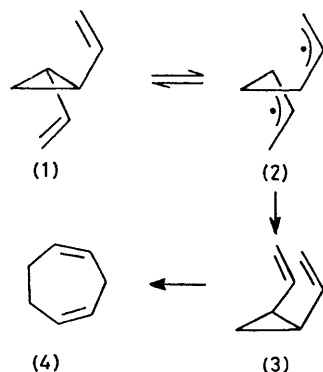
## Thermal Decomposition of Bicyclic Divinyl- $\Delta^1$ -pyrazolines and Divinylcyclopropanes

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**Summary** The thermal decomposition of bicyclic divinylcyclopropanes and bicyclic divinyl- $\Delta^1$ -pyrazolines leads to identical products, suggesting a common reaction pathway.

THE thermal rearrangement of *trans*-divinylcyclopropane (**1**) proceeds either through a diradical intermediate (**2**)<sup>1</sup> (Scheme 1), or alternatively *via* a one centre epimerization



SCHEME 1.

process, by-passing the diradical intermediate.<sup>2</sup> They both lead to *cis*-divinylcyclopropane (**3**), which undergoes a rapid Cope rearrangement to cyclohepta-1,4-diene (**4**).<sup>3</sup> Both mechanisms have been claimed to accommodate the observed isomerization and racemization rates. However they are complicated by the fact that they lead to identical (Cope) reaction products, *e.g.* (**4**).

The observation of 'non-Cope' reaction products should be possible in the thermolysis of the bicyclic divinylcyclopropane (**8**), and (using an independent approach) the bicyclic  $\Delta^1$ -pyrazoline (**5**), if diradical intermediates are involved (Scheme 2).

Compound (**5**) was prepared *via* 1,3-dipolar cycloaddition of 3-diazoprop-1-ene to cyclohexa-1,3-diene (neat liquids, +4 °C, 4 days) and purified by low temperature column chromatography on Florisil (n-pentane-ether).<sup>†</sup> It decomposes thermally between 30 and 65 °C to produce (**8**), (**9**), and (**10**).<sup>‡</sup> Yields at 45 °C are: 36.1 ± 0.4 (**8**), 62.9 ± 0.6 (**9**), and 1.0 ± 0.1% (**10**); at 65 °C: 36.5 ± 0.4 (**8**), 62.5 ± 0.6 (**9**), and 1.0 ± 0.1% (**10**).

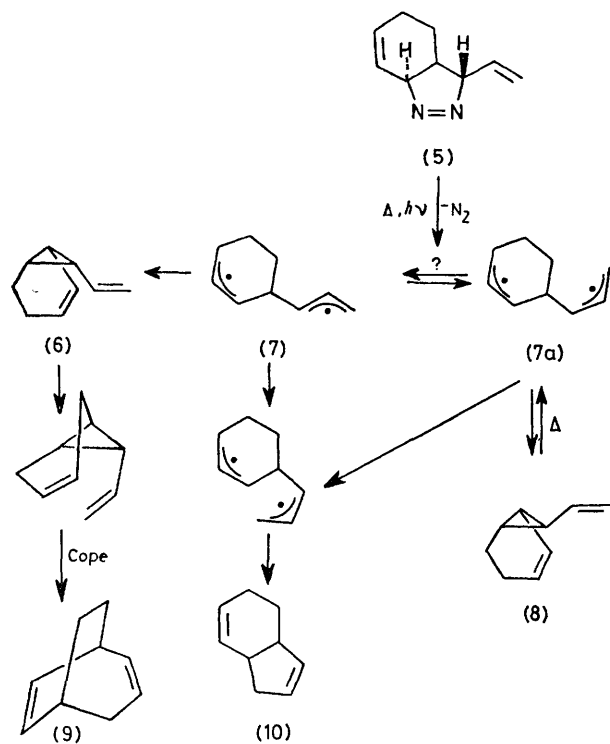
The decomposition of (**5**) follows first-order kinetics§ (10<sup>4</sup> k/s<sup>-1</sup> = 9.80 at 49.5 °C;  $\Delta H^\ddagger$  = 23.0 ± 0.7 kcal mol<sup>-1</sup>;  $\Delta S^\ddagger$  = 0.4 ± 2.5 cal K<sup>-1</sup> mol<sup>-1</sup>). The data indicate, in reference to *trans*-3,5-dimethyl- $\Delta^1$ -pyrazoline ( $\Delta H^\ddagger$  = 40 kcal mol<sup>-1</sup>)<sup>4a</sup> and 3-vinyl- $\Delta^1$ -pyrazoline ( $\Delta H^\ddagger$  = 31 kcal

<sup>†</sup> Compound (**5**) gave satisfactory analytical and spectroscopic data; the stereochemistry was assigned by comparison of the n.m.r. spectrum with that of the corresponding methyl compound.

<sup>‡</sup> All compounds were identified spectroscopically and/or by comparison with literature data; (**9**): M. V. Moncur and J. B. Grutzner, *J. Amer. Chem. Soc.*, 1973, **95**, 6449; (**10**): J. Japenga, M. Kool, and G. W. Klumpp, *Tetrahedron Letters*, 1974, 3805. Yields were all determined by v.p.c.

§ Rates were measured by following the decay of the  $n-\pi^*$  u.v. transition of (**5**) at 336 nm between 29.8 and 68.0 °C. Good first order plots were obtained and the reactions were followed for > 10 half-lives.

$\text{mol}^{-1}$ ),<sup>4b</sup> a contribution of 8–9  $\text{kcal mol}^{-1}$  per vinyl group towards a lowering of the activation enthalpy. This value is close to the delocalization energy of an allylic radical,<sup>5</sup> thus suggesting the simultaneous cleavage of both C–N bonds in (5) with formation of the diallylic 1,3-diradical (7).



SCHEME 2.

Support for formation of (7) is also derived from the formation of small, but significant, amounts of (10). Its formation involves the intermediacy of the diradical (7a), which can be derived from the rotational isomers of (5) or

(8) (Scheme 2), or from (7) with loss of delocalization to overcome the rotational barrier of the allylic radical. Both processes are disfavoured<sup>1,5</sup> in comparison to ring closure to (6) and (8); however they give an indication of a diradical intermediate.

The rapid reaction (6)  $\rightarrow$  (9) in the thermolysis of (5) precludes the detection of (6). Photolysis of (5) at  $-45^\circ\text{C}$  in the probe of an n.m.r. spectrometer (Bruker HX90R with modified probe for direct irradiation, Philips SP1000 lamp, Pyrex filter) produces  $61.8 \pm 0.6$  (8),  $36.0 \pm 0.4$  (6), and  $2.2 \pm 0.2\%$  (10)<sup>†</sup> [analysed by v.p.c. after the rearrangement (6)  $\rightarrow$  (9)]. The Cope rearrangement (6)  $\rightarrow$  (9) proceeds under conditions similar to those for (3)<sup>3</sup> and can be followed between 0 and  $20^\circ\text{C}$  by careful n.m.r. integration.

Thermolysis of (8) in the gas phase at  $160^\circ\text{C}$  ( $10^4 \text{ k/s}^{-1} = 2.75$ ) produces  $99.2 \pm 1$  (9) and  $0.8 \pm 0.1\%$  (10). These results indicate, that the thermal ring-opening reaction of (8) produces [via (7) and/or (7a)] the *cis*-divinylcyclopropane (6), which leads via an irreversible rapid Cope rearrangement to (9). Compound (9) is stable up to  $250^\circ\text{C}$  as shown by control experiments. The amount of (10) produced is practically identical with that obtained in the decomposition of (5).

The identity in the decomposition patterns of (5) and (8), the concerted bond cleavage in the thermolysis of (5), and the formation of (10) all suggest a common diradical intermediate in the thermolysis of (5) and (8). The participation of a 1,3-sigmatropic pathway for the formation of (10) from (8) cannot be excluded completely. Our results seem to support a diradical mechanism, which has been proposed for the rearrangement of (1).<sup>1,6</sup>

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<sup>1</sup> M. Arai and R. J. Crawford, *Canad. J. Chem.*, 1972, **50**, 2158.

<sup>2</sup> J. E. Baldwin and C. Ullenius, *J. Amer. Chem. Soc.*, 1974, **96**, 1542.

<sup>3</sup> The rearrangement (3)  $\rightarrow$  (4) has been measured quantitatively: J. M. Brown, B. T. Golding, and J. J. Stofko, jun., *J.C.S. Chem. Comm.*, 1973, 319; M. Schneider, *Angew. Chem. Internat. Edn.*, 1975, **14**, 707.

<sup>4</sup> (a) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 1966, **88**, 3963; (b) R. J. Crawford and D. M. Cameron, *Canad. J. Chem.*, 1967, **45**, 691.

<sup>5</sup> W. v. E. Doering and G. H. Beasley, *Tetrahedron*, 1973, **29**, 2231; W. R. Roth, G. Ruf, and P. W. Ford, *Chem. Ber.*, 1974, **108**, 48.

<sup>6</sup> For a recent review see: J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jenkins, *J. Amer. Chem. Soc.*, 1976, **98**, 5937.