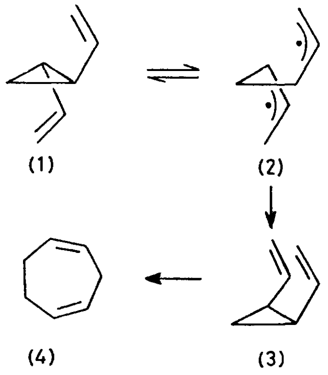
Thermal Decomposition of Bicyclic Divinyl-Δ¹-pyrazolines and Divinylcyclopropanes

By MANFRED P. SCHNEIDER* and BERND CSACSKO
(*Institut für Chemie, Universität Hohenheim,* D-7000 *Stuttgart*-70, *Germany*)

Summary The thermal decomposition of bicyclic divinylcyclopropanes and bicyclic divinyl-Δ¹-pyrazolines leads to identical products, suggesting a common reaction pathway.

THE thermal rearrangement of *trans*-divinylcyclopropane (**1**) proceeds either through a diradical intermediate (**2**)[1] (Scheme 1), or alternatively *via* a one centre epimerization process, by-passing the diradical intermediate.[2] They both lead to *cis*-divinylcyclopropane (**3**), which undergoes a rapid Cope rearrangement to cyclohepta-1,4-diene (**4**).[3] 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**).



SCHEME 1.

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 Δ¹-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).† It decomposes thermally between 30 and 65 °C to produce (**8**), (**9**), and (**10**).‡ 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§ ($10^4\,k/\mathrm{s}^{-1} = 9{\cdot}80$ at 49·5 °C; $\Delta H^{\ddagger} = 23{\cdot}0 \pm 0{\cdot}7$ kcal mol^{-1}; $\Delta S^{\ddagger} = 0{\cdot}4 \pm 2{\cdot}5$ cal K^{-1} mol^{-1}). The data indicate, in reference to *trans*-3,5-dimethyl-Δ¹-pyrazoline ($\Delta H^{\ddagger} = 40$ kcal mol^{-1})[4a] and 3-vinyl-Δ¹-pyrazoline ($\Delta H^{\ddagger} = 31$ kcal

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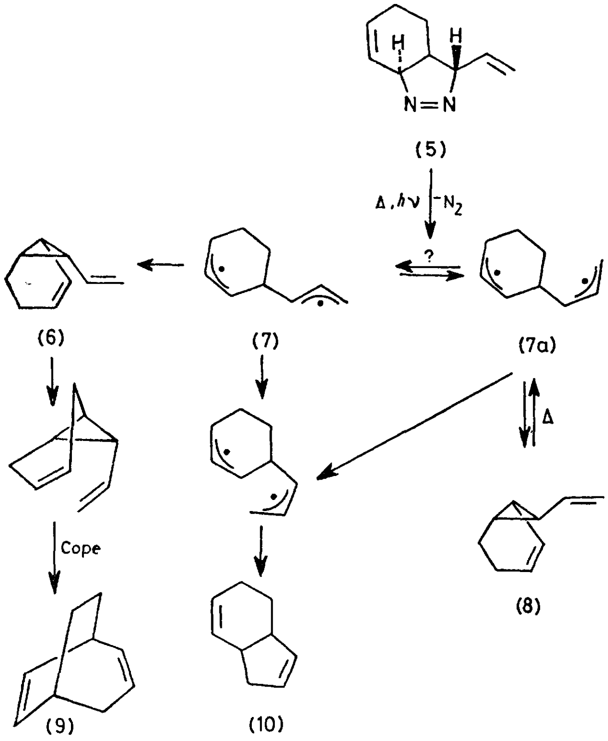
† Compound (**5**) gave satisfactory analytical and spectroscopic data; the stereochemistry was assigned by comparison of the n.m.r. spectrum with that of the corresponding methyl compound.

‡ 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–π^* 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-lifes.

mol^{-1}),[4b] a contribution of 8—9 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,[5] 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[1,5] in comparison to ring closure to (**6**) and (**8**); however they give an indication of a diradical intermediate.

The rapid reaction (**6**) → (**9**) in the thermolysis of (**5**) precludes the detection of (**6**). Photolysis of (**5**) at −45 °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 ± 0·6 (**8**), 36·0 ± 0·4 (**6**), and 2·2 ± 0·2% (**10**)‡ [analysed by v.p.c. after the rearrangement (**6**) → (**9**)]. The Cope rearrangement (**6**) → (**9**) proceeds under conditions similar to those for (**3**)[3] and can be followed between 0 and 20 °C by careful n.m.r. integration.

Thermolysis of (**8**) in the gas phase at 160 °C ($10^4\,k/\text{s}^{-1} = 2{\cdot}75$) produces 99·2 ± 1 (**9**) and 0·8 ± 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 °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**).[1,6]

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[3] The rearrangement (**3**)→(**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.

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