Thermolysis of *syn*- and *anti*-Dimers of Cyclobutadiene

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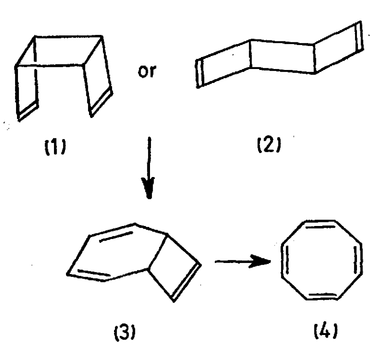
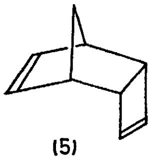
Summary Arrhenius parameters have been obtained for the thermolysis of *syn*- and *anti*-dimers of cyclobutadiene, and the data explained in terms of a biradical mechanism; the possibility that the singlet biradical may undergo intersystem crossing is discussed.

THE thermal isomerization of bicyclic cyclobutenes is still a mechanistic problem.[1] We have been studying the pyrolysis of a number of highly strained cyclobutenes. A recent communication[2] prompts us to report our results on the thermal behaviour of (**1**) and (**2**) in the gas phase. Both compounds yield cyclo-octatetraene, with the valence isomer (**3**) being a probable intermediate. Compound (**1**) isomerizes between 90 and 121 °C by a homogeneous first-order process which is almost certainly unimolecular. The rate constants were determined at each of 9 temperatures, from first-order plots, using analytical data obtained by gas chromatography, and yielded the Arrhenius equation (1).

$$\log k_1/\mathrm{s}^{-1} = 14{\cdot}22 \pm 0{\cdot}09 - (30{\cdot}49 \pm 0{\cdot}16 \text{ kcal mol}^{-1}/RT \ln 10)\dagger \quad (1)$$

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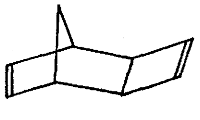
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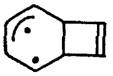
(7)

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† All errors are standard deviations.

Similarly the ***anti***-isomer (**2**) yielded the Arrhenius equation (2) for runs carried out between 112 and 146 °C.

$$\log k_2/\mathrm{s}^{-1} = 14{\cdot}01 \pm 0{\cdot}09 - (32{\cdot}59 \pm 0{\cdot}17\ \mathrm{kcal\ mol^{-1}}/RT \ln 10) \qquad (2)$$

The difference in energies of activation, ΔE_a (2·1 kcal mol^{-1}) can be rationalised as due to the difference in strain energy between (**1**) and (**2**). It appears unnecessary to involve the relatively large (*ca.* 0·4 eV, shown by photoelectron spectroscopy[3]) repulsive through-space interaction of the π-bonds in (**1**). We therefore suggest that the difference in energies of activation of 3·7 kcal mol^{-1} between (**5**) and (**6**) may also be entirely due to differences in ground-state energies, since there is the same through-space interaction[4] in (**5**) as in (**1**). The increase from 2·1 to 3·7 kcal mol^{-1} may arise because the distance between the *endo*-hydrogen (on C-9) and the 3,4-π bond in (**6**) becomes smaller as the cyclobutene ring opens in a disrotatory fashion, hence increasing the non-bonded interaction.

Our data do not agree well with those reported recently.[2] While for (**2**) the Arrhenius parameters agree separately within their quoted errors, our values will lead to systematically lower rate constants at all temperatures. For compound (**1**) the Arrhenius parameters reported by Dewar *et al.*[2] of $\log A/\mathrm{s}^{-1} = 13{\cdot}36 \pm 0{\cdot}34$ and E_a/kcal mol^{-1} = 28·8 ± 0·6 do not agree within the combined quoted errors, but here the effects are compensatory and the discrepancy in the rate constants quite small. Dewar ***et al.*** suggest, as a result of MINDO/3 calculations, that (**1**) cannot yield (**3**) by a singlet concerted process (they calculate an E_a of 57·7 kcal mol^{-1}). A triplet pathway, for which they calculate an E_a of 36·0 kcal mol^{-1} is therefore suggested.

We find it difficult to reconcile a major direct triplet pathway with the positive entropy of activation for the isomerization of both (**1**) and (**2**). The observed Arrhenius parameters are consistent with a biradical mechanism. Further, the energy difference between the singlet and triplet states of the biradical (**7**) will be small and some of the singlet species might well undergo intersystem crossing.

Such a mechanism would produce a triplet component of the reaction. Since the recyclization of (**7**) to (**1**) or (**2**) must have a high E_a (*ca.* 15 kcal mol^{-1}) and therefore be a relatively slow process, the formation of (**3**) from (**7**) will be relatively fast and, even if it involves a triplet pathway, the entropy of activation of the overall reaction will be unaffected. Whether the triplet component of the reaction is a major or a minor one, will, on our mechanism, depend on the relative rates of intersystem crossing and the rate of reaction (**7**) → (**3**).

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[2] R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegir, *J. Amer. Chem. Soc.*, **1975**, **96**, **7581**.

[3] R. Gleiter, E. Heilbronner, M. Hekman, and H.-D. Martin, *Chem. Ber.*, **1973**, **106**, 28.

[4] H.-D. Martin, S. Kagabn, and R. Schwesinger, *Chem. Ber.*, in the press.