Communications to the Editor

Dimerization of Butadiene

Sir:

The dimerization of 1,3-butadiene has occupied a prominent position in many studies of the Diels-Alder reaction. Controversy in this area has centered around two limiting mechanisms: a concerted $_{\pi}4_s + _{\pi}2_s$ cycloaddition and pathways involving the intermediacy of bisallyl diradicals.[1] Estimates of the highest energy point along the diradical pathway are within 1-2 kcal/mol of the observed activation energy for the dimerization. Unfortunately the errors associated with such thermochemical estimates are also 1-2 kcal/mol, and firm mechanistic conclusions by this method are untenable in the present case. We have chosen to use the sensitive probe of stereochemistry to study this simple Diels-Alder reaction, and we wish to report here our analysis of the thermal dimerization[2] of *cis,cis*-1,4-dideuterio-1,3-butadiene.[3] The relative deuterium stereochemistry in the major (92%) product, vinylcylohexene, has been determined. Neither limiting mechanism is supported by our results, and we shall argue that the best explanation of the data consists of a mixture of both allowed and forbidden 4 + 2 cycloadditions.

Products anticipated from reaction by both concerted and diradical mechanisms are shown[4] in Figure 1. Retention of the cis configuration at the terminal vinyl group is predicted by each mechanism and is observed.[5] Absence of scrambling at this center indicates that there is no isomerization of the butadiene before dimerization. This is confirmed by noting that butadiene recovered after dimerization and analyzed[3a] by Raman spectroscopy is isomerically unchanged.

To determine the relative deuterium stereochemistry at the other three centers, the vinylcyclohexene was converted[6] (Figure 2) to *exo*-2-hydroxy-7-oxabicyclo[3.2.1]octane (**1**). In the presence of 60 mol % Eu(DPM)$_3$ the ^{1}H NMR spectrum of **1** is adequately resolved over 15 ppm. Integration of the spectrum of **1**, obtained ultimately from the products of the dimerization of *cis,cis*-dideuteriobutadiene, gives information concerning the endo to exo ratio (H$_e$ and H$_f$) and C$_5$-C$_6$ bond rotation (H$_i$ and H$_k$). The predicted and observed values for proton integration are given in Table I. The results indicate no particular preference for endo or exo pathways.[7] Of greater significance is the observation[8] of 10% stereoisomeric scrambling between C$_5$ and C$_6$.

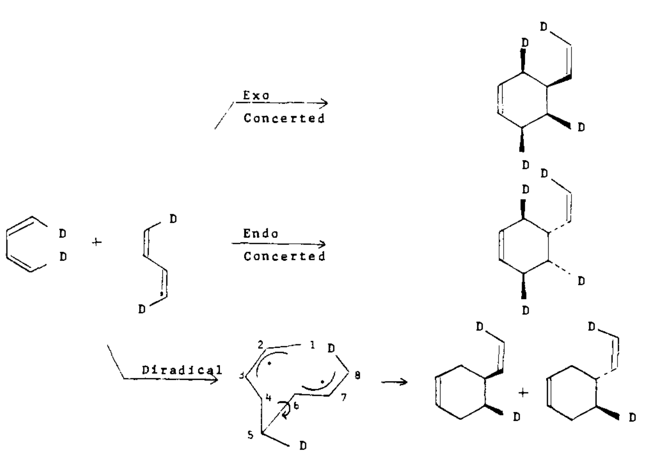

Figure 1. Anticipated products from concerted and diradical reactions. Only a single enantiomer for each product is shown. To simplify the drawing the C$_1$ and C$_4$ deuteria in the diradical products are also omitted.[4]

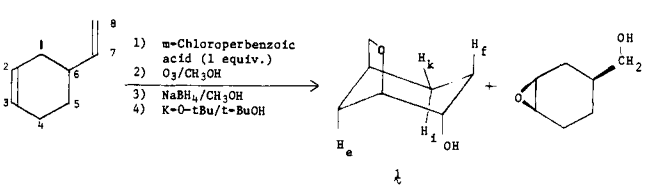

Figure 2. Conversion of vinylcyclohexene to *exo*-2-hydroxy-7-oxabicyclo[3.2.1]octane (**1**).

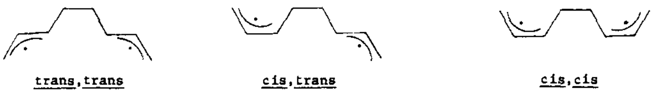

Figure 3. The three isomeric diradicals from butadiene.

Table I. Expected and Observed ^{1}H NMR Integrated Intensities for 1 Originating from *cis,cis*-Dideuteriobutadiene

	H$_e$	H$_f$	H$_i$	H$_k$
Exo concerted	1.0	0.0	1.0	0.0
Endo concerted	0.0	1.0	1.0	0.0
Freely rotating diradical	*b*	*b*	0.5	0.5
Observed[a]	0.5	0.5	0.9	0.1

[a] Observed in the presence of 60 mol % Eu(DPM)$_3$. [b] See ref 4.

A simple explanation for these results might be formulated in terms of a mixture of diradical and concerted mechanisms. The results would then require 20% of a diradical species if rotational equilibration about C$_5$-C$_6$ occurs before ring closure or an even higher proportion of a diradical if ring closure and C$_5$-C$_6$ bond rotation are competitive.

This interpretation can be discounted as inconsistent with the product ratio for the dimerization. To illustrate, butadiene can dimerize to three isomeric diradicals depending on the conformation of the reacting species (Figure 3). Cyclohexene products can be formed only if at least one of the allyl units is in the cis conformation; the trans,trans diradical can only lead to cyclobutane products. In all cases, product formation from the diradical is kinetically favored over reversion to butadiene.[1] The chemical consequences which could then be associated with the trans,trans diradical[9] amount to less than 8% of the product mixture. If one makes the well-precedented assumption[10] that the trans,trans diradical is the most rapidly formed of the three diradical species, then an explanation of the scrambling of stereochemistry based on diradicals becomes unsatisfactory. It is inconsistent to require that more than 20% of the vinylcyclohexene be formed from the cis,trans and cis,cis diradicals while less than 8% of the product arises from the most easily formed trans,trans diradical.

The results require mechanisms which will account for the high reactivity of cisoid butadiene while allowing some scrambling of stereochemistry. These requirements are most easily accommodated by invoking both the suprafacial (90%) and antarafacial (10%) participation of the dienophile in concerted reactions. Operationally this allows bond

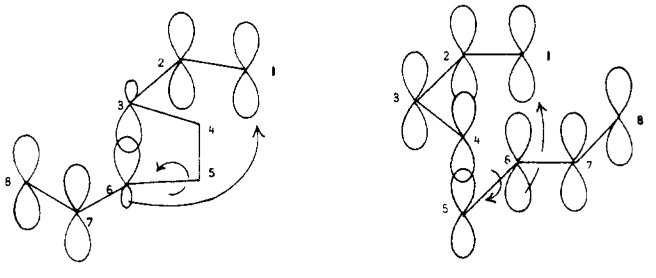

Figure 4. A comparison of the motion required for inversion of configuration at C_6 in the divinylcyclobutane pyrolysis and the butadiene dimerization.[13]

formation between C_1 and C_6 with both retention and inversion of stereochemistry at C_6, while the continuous overlap of orbitals provides a rationale for the high cisoid butadiene reactivity.

Since endo and exo products cannot be separated, the mode of cycloaddition to the diene cannot be distinguished. The requirement of 10% antarafacial addition to the dienophile is thus consistent with either allowed ${}_\pi4_a + {}_\pi2_a$ or forbidden ${}_\pi4_s + {}_\pi2_a$ reactions.

While the doubly antarafacial mechanism cannot be eliminated, this result would be without precedent.[11] On the other hand, analogous mixtures of allowed and forbidden processes are already documented for the C_8H_{12} surface. Pertinent to the present work are Berson's studies of divinylcyclobutane pyrolyses.[12] Migration of C_6 to C_1 in *trans*-divinylcyclobutane occurs with both inversion (allowed) and retention (forbidden) of configuration at C_6. The inversion involves rotation about C_5–C_6 a motion similar to that required for the stereoisomeric scrambling observed in the dimerization[13] (Figure 4).

This reaction joins a now substantial number of transformations for which thermochemical analysis suggests energetically accessible diradical surfaces, but which possess weak bonding interactions which control the product ratios.[12] A feature which may be general to such situations is the existence of both allowed and forbidden mechanisms which are favored energetically relative to diradicals.[15] Many 1,3-sigmatropic migrations are thought to exhibit this property, and we believe such an explanation forms the best basis for understanding the butadiene dimerization.

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References and Notes

(1) (a) W. von E. Doering, M. Frank-Newmann, D. Hasselman, and R. K. Kaye, *J. Am. Chem. Soc.*, **94**, 3833 (1972); (b) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967); (c) J. A. Berson and P. B. Dervan, *J. Am. Chem. Soc.*, **95**, 267 (1973).

(2) Reactions were run in degassed and sealed Pyrex tubes at 136°C for ~20 hr. This dimerization yielded 92% vinylcyclohexene, 5% divinylcyclobutane, and 2% cyclooctadiene, the latter most likely via Cope rearrangement of *cis*-divinylcylobutane. After the products are heated an additional 12 hr at 136°, the product ratios change <1% and the deuterium stereochemistry in the vinylcyclohexene is unaffected.

(3) (a) L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 8620 (1972); (b) L. M. Stephenson and R. V. Gemmer, submitted for publication. (c) The diene used in this study showed no detectable isomeric impurity by Raman spectroscopy under conditions known to be capable of detecting 1–2% cis,trans or trans,trans diene contaminant.[3a] The diene mass spectrum and a detailed analysis of the carbon spectrum of the resulting vinylcyclohexene confirm that the starting material is >99% d_2.

(4) In this paper we use a numbering system based on the diradical (see Figure 1); this system is also used to describe the vinylcyclohexene (see Figure 2). The stereochemistry at C_1 and C_4 in the product from the diradical is determined by endo and exo like approach which leads to threo and erythro intermediates. Bond rotation about C_5–C_6 plus at least one other rotation is necessary to scramble this relationship.

(5) The ^{1}H NMR at 60 MHz shows a doublet at δ 4.9, $J = 11$ Hz. The trans coupling constant is 17 Hz and would be easily observed.

(6) The structure of **1** and the assignment of each proton resonance was determined from proton decoupling experiments on perprotio-**1** and trideuterio-**1** (available from D_2O exchange of the corresponding ketone followed by LiAl(O-*t*-Bu)$_2$D$_2$ reduction) in the presence of shift reagent. The cis epoxy alcohol is easily separated from **1** by preparative GLC on Carbowax 20M, 20% on Chrom G, 10 in.

(7) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046, 4388 (1965); (b) W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).

(8) This observed scrambling between C_5 and C_6 is the result of three separate determinations. In one of these experiments a mixture of dienes, 90% cis,cis and 10% trans,trans, was employed. This peak enhancement experiment resulted in an integrated intensity of 0.2 protons for H_k, as expected.

(9) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965); C. A. Stewart, *ibid.*, **94**, 635 (1972).

(10) To our knowledge, all thermal cycloadditions of butadiene known to proceed via a diradical intermediate give products derived predominantly, in some cases almost exclusively, from trans allyl radical units (cf. P. D. Bartlett and J. S. Swenton, *J. Am. Chem. Soc.*, **90**, 2056 (1968) and ref 1a).

(11) This possibility has previously been proposed. Unfortunately the system carried too few labels for the conclusion to be certain. E. E. van Tamelen and J. W. Murphy, *J. Am. Chem. Soc.*, **92**, 7204 (1970).

(12) (a) J. A. Berson, *Acc. Chem. Res.*, **1**, 152 (1968); (b) *ibid.*, **5**, 406 (1972); (c) J. A. Berson and P. B. Dervan, *J. Am. Chem. Soc.*, **95**, 269 (1973); (d) J. A. Berson and R. W. Holder, *ibid.*, **95**, 2037 (1973).

(13) Our representation of this mechanism in Figure 4 implies the prior formation of the C_4–C_5 bond followed by rapid ring closure. This possibility is reminiscent of the two-stage mechanism[14] with the added feature that the concerted ring closure can be either allowed or forbidden.

(14) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(15) (a) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94**, 8917 (1972); (c) N. D. Epiotis, *ibid.*, **94**, 1924 (1972); (c) W. Schmidt, *Tetrahedron Lett.*, 581 (1972), and ref 12b.

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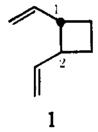
Stereochemistry of the Diels–Alder Dimerization of *trans,trans*-Penta-1,3-diene-*1-d*[1]

Sir:

A mechanistic energy surface based upon the thermochemical and kinetic data for the formation of 4-vinylcyclohexene (**2**) by the thermal rearrangement of *trans*-1,2-divinylcyclobutane (**1**) and by the Diels–Alder dimerization of buta-1,3-diene (**3**) proposes[2,3] that neither reaction is concerted, but that each is a stepwise process passing over a common biradical intermediate. Hypothetically, this biradical would be formed by cleavage of the C_1–C_2 bond of **1**, or by juncture at C_1 of two molecules of **3**. Another analysis of the data leads to the conclusion, "It is clear that the magnitude of concert in this Diels–Alder reaction, if it be not zero, is at best small."[4] If concert is weak in the diene dimerizations, a concerted mechanism with an orbital topology other than $2_s + 4_s$ or a biradical mechanism might result in a violation[7,8] of the familiar[9,10] suprafacial-on-the-dienophile, suprafacial-on-the-diene rule.



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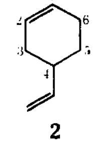

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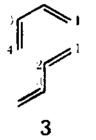

3

The exo and endo dimers of *trans*-piperylene (**4a**, *trans*-penta-1,3-diene) are separable diastereomers (**5a** and **6a**),