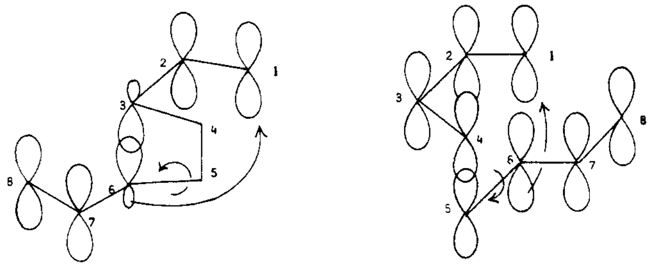

Figure 4. A comparison of the motion required for inversion of configuration at C_6 in the divinylcyclobutane pyrolysis and the butadiene dimerization.[13]

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 $_{\pi}4_a + {}_{\pi}2_a$ or forbidden $_{\pi}4_s + {}_{\pi}2_a$ 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.

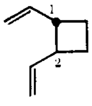
(16) Address correspondence to this author at the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

L. M. Stephenson,* [16] **Robert V. Gemmer, Steven Current**
Department of Chemistry, Stanford University
Stanford, California 94305
Received May 5, 1975

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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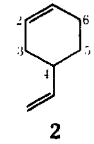

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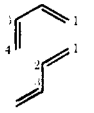
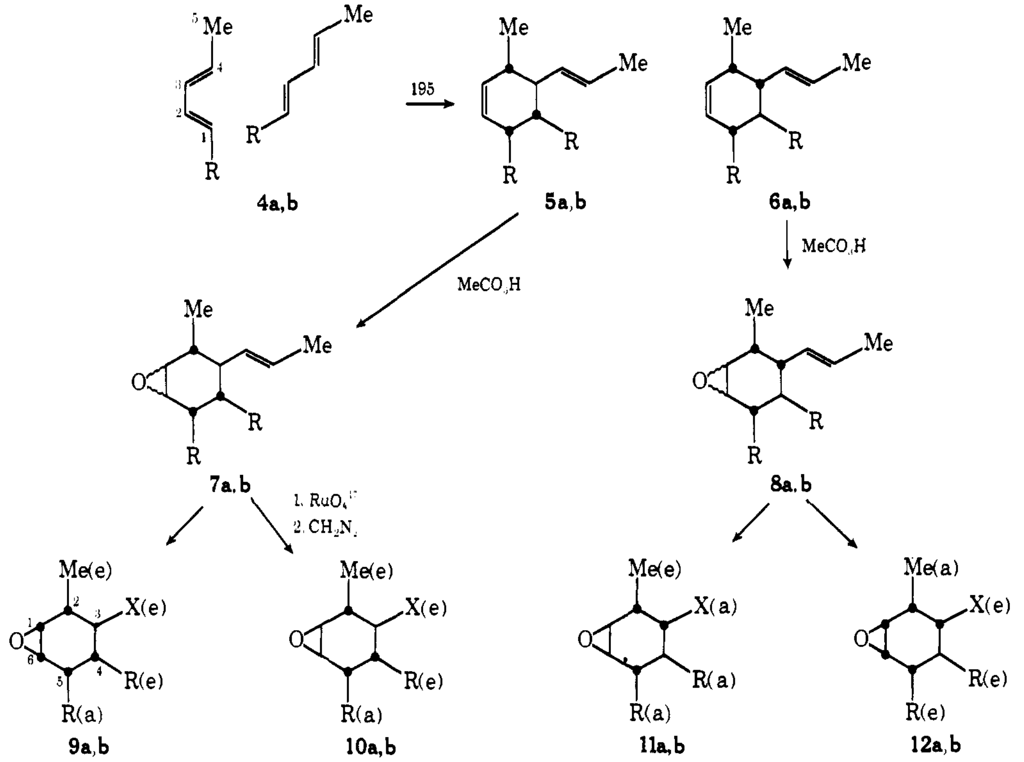


3

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



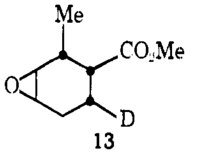
[a] Key: a, R = H; b, R = D; X = CO_2Me.

and insertion of a deuterium label at C_1 of piperylene permits the complete analysis of the Diels–Alder stereochemistry.[11] Scheme I shows the configurations of each dimeric isomer (**5b** and **6b**) if the dimerization of *trans,trans*-penta-1,3-diene-*1-d* (**4b**) were exclusively suprafacial on the diene and, respectively, suprafacial-exo and suprafacial-endo on the dienophile.

Reduction of *trans*-pent-3-ene-1-yne[12] with dicyclohexylborane, followed by deuterolysis with CH_3CO_2D[13] give stereospecifically *trans,trans*-penta-1,3-diene-*1-d* (**4b**, Scheme I) containing 90 ± 2% of one deuterium at the trans-1 position (^{1}H NMR analysis). Thermal dimerization of **4b** at 195° gives 82% of the "ortho" dimers (**5b** and **6b**, in a 45:55 ratio), 11% of "meta" dimer, 6% of *cis*-3,4-dimethylcycloocta-1,5-diene, and 1% of *trans*-3,4-dimethylcycloocta-1,5-diene.[14,15]

Gas chromatography (GC, 20% FFAP column, 125°) separates **5b** and **6b**. The deuterium content of the dimers and the other compounds in the series is established by direct ^{2}H NMR[18] ($CDCl_3$ internal standard) as 90 ± 2% of 2D, and by combustion analysis (falling drop)[19] as 87.7 ± 1% of 2D.

The chemical transformations shown in Scheme I convert **5b** and **6b** to four epoxy esters in pairs, **9b–10b**, and **11b–12b**, from which **9b**, **10b**, and **12b** are isolated by GC.[20] Independent stereospecific syntheses of the undeuterated analogs **9a–12a**[21] and the 4-deuterio-5-protio analogs **13** and **14**[23] provide model compounds for the conformational (e = equatorial, a = axial) and hence configurational assignments of Scheme I. Spin decoupling experiments on samples treated with tris(heptafluorodimethyloctandione)europium ($Eu(fod)_3$)[25] facilitate the assignments by correlation of large (10–11 Hz) and small (2–3 Hz) coupling constants with vicinal H_a–H_a and H_a–H_e (or H_e–H_e) groups, respectively.[26] It is then easy to recognize deuterium incorporation at specific sites in the deuterated series. A typical set of data, obtained on **10b** at a $Eu(fod)_3$/substrate ratio of 0.40 in CCl_4 solution, follows (proton, chemical shift in δ units, integrated intensity): H_6, 8.95, 1.04; H_1, 8.47, 1.02; H_{2a} + H_{4a}, 7.15, 1.98; H_{5e}, 5.60, 1.00; H_{3a} + CO_2Me, 5.23, 3.93; H_{4e}, 4.40, 0.14; H_{5a}, 3.80, 0.11; Me, 2.66, (3.00).



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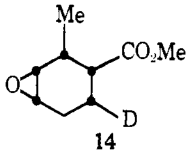

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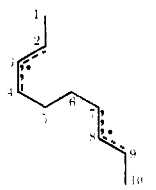
These proton data and similar observations on **9b** and **12b** establish that, in all three compounds, the extents of D labeling in the C_4 position trans to CO_2Me and in the C_5 position cis to Me are identical with each other and essentially 100% of the maximum permitted by the total deuterium incorporation.

Both continuous wave[18] and Fourier transform[27] direct ^{2}H NMR spectroscopy of **9b** and **10b** in CCl_4 solutions containing $Eu(fod)_3$, show two approximately equal resonances at chemical shifts corresponding to positions 4e and 5a and no detectable (<2%) absorption at positions 4a or 5e, or elsewhere. This fully confirms the ^{1}H spectroscopic results.

With reference to Scheme I, the data may be interpreted as exclusive suprafacial-on-the-diene, suprafacial-on-the-dienophile addition in both the exo and endo Diels–Alder modes in the dimerization of piperylene. Of the imaginable concerted Diels–Alder dimerizations, only the $2_s + 4_s$ pathway is consistent with the observed stereochemistry at the diene and dienophile sites. Although cyclization in a biradical intermediate at a rate much faster than internal rotation might be said to simulate the same stereochemical result, it would be necessary to postulate that only those biradicals born in a coiled conformation (**16**) could cyclize. In those born in an extended conformation (**15**), an internal rotation about the C_5–C_6 bond would be required for cyclization, and one then would expect configuration-destroying rotation about the C_6–C_7 bond also. For the present, the con-



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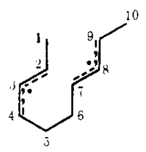

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certed mechanism offers a simpler interpretation.

The previous finding[16] that the rearrangement of *trans*-1,2-*trans,trans*-dipropenylcyclobutane to **5a** and **6a** occurs with a slight predominance of *inversion* of configuration at the migrating group, when combined with the present observation of *complete retention* at the same site (the dienophile) in the Diels-Alder dimerization, excludes a common intermediate for the two reactions.

References and Notes

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the National Science Foundation for partial support by grant GP33909*X*.

(2) S. W. Benson, *J. Chem. Phys.*, **46,** 4920 (1967).

(3) The suggestion[2] of a biradical mechanism for the Diels–Alder dimerization of butadiene recalls a similar proposal in the case of isoprene.[5,6]

(4) W. v.E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Am. Chem. Soc.*, **94,** 3833 (1972).

(5) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80,** 5819 (1958).

(6) See, however, G. Jenner, *Angew. Chem., Int. Ed. Engl.*, **14,** 137 (1975); J. Rimmelin and G. Jenner, *Tetrahedron*, **30,** 3081 (1974).

(7) For apparent exceptions[8] to the cis-on-the-dienophile rule, see V. Mark, *J. Org. Chem.*, **39,** 3179, 3181 (1974).

(8) See, however, W. Shih, N. Lau, and S. Seltzer, *J. Org. Chem.*, **40,** 1269 (1975), footnote 16b.

(9) For reviews, see (a) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5,** 211 (1966); **6,** 16 (1967); (b) A. Wassermann, "The Diels-Alder Reaction", Elsevier, Amsterdam, 1965, p 26; (c) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, p. 739; (d) A. Onishchenko, "Diene Synthesis", Israel Program for Scientific Translation, Jerusalem, 1964, p 35.

(10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, p 65 ff.

(11) For a report on the dienophile stereochemistry in the dimerization of *trans,trans*-**3**-*1,4*-d_2, see L. M. Stephenson, R. V. Gemmer, and S. Current, *J. Am. Chem. Soc.*, preceding paper in this issue.

(12) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950); 3314 (1953).

(13) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Am. Chem. Soc.*, **93,** 3395 (1971).

(14) This product distribution is in good agreement with that reported by I. N. Nazarov, N. V. Kuznetsov, and A. I. Kuznetsova, *Zh. Obshch. Khim.*, **25,** 320 (1955).

(15) Compounds **5a** and **6a** in the unlabeled series are identified by comparison with synthetic authentic samples.[16]

(16) J. A. Berson and P. B. Dervan, *J. Am. Chem. Soc.*, **95,** 269 (1973).

(17) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33,** 1701 (1955).

(18) By Mr. Walter Krol, using the Bruker-270 system.

(19) By Mr. Josef Nemeth, Urbana, Ill.

(20) Preparative GC on a 3 m × 10 mm 20% Carbowax 20M on Chromosorb W 60–80 at 190°; analytical GC on a 35 m XE 60 capillary column at 100°.

(21) Prepared from the known[16,22] methyl *trans*- and *cis*-2-methylcyclohex-3-ene-1-carboxylates and characterized by elemental analyses and NMR spectra.

(22) K. Alder and W. Vogt, *Justus Liebigs Ann. Chem.*, **564,** 120 (1949).

(23) By epoxidation of the adducts from *trans*-piperylene and methyl acrylate-*cis-3-d*.[24]

(24) R. K. Hill and G. R. Newton, *J. Org. Chem.*, **34,** 740 (1969).

(25) (a) R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93,** 1522 (1971); (b) A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73,** 553 (1973); (c) P. E. Manni, G. A. Howie, B. Katz, and J. M. Cassidy, *J. Org. Chem.*, **37,** 2769 (1972).

(26) (a) M. Karplus, *J. Am. Chem. Soc.*, **85,** 2870 (1963); (b) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, Inc., San Francisco, Calif., 1964, p 49 ff.

(27) We are indebted to Professor C. H. DePuy and Mr. Ashley of the University of Colorado for the Fourier transform spectra, which were taken with the Varian XL-100 system.

(28) Supported by a postdoctoral fellowship from the Stiftung für Stipendien auf dem Gebiete der Chemie, Basel, Switzerland.

Jerome A. Berson,* Roger Malherbe[28]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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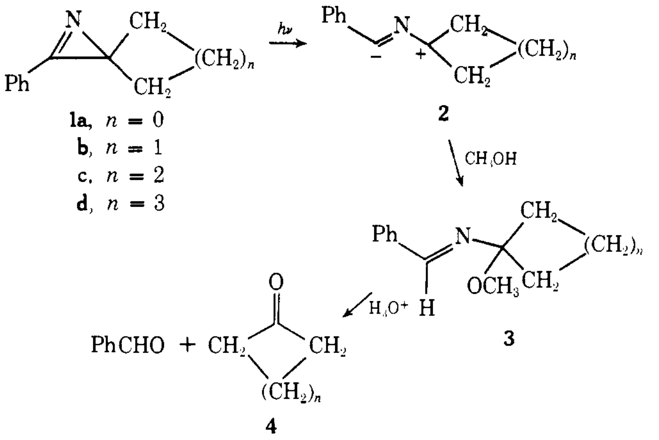
Generation of 2-Phenylazirinylidene from the Photolysis of 2-Phenyl-1-azaspiro[2.2]pent-1-ene[1]

Sir:

In order to rationalize the intriguing photochemical cycloadditions that arylazirines undergo with electron-deficient olefins, we proposed the intervention of a nitrile ylide intermediate.[2,3] As a 1,3-dipole, this species can be intercepted with a variety of dipolarophiles to form five-membered rings.[4-9] In addition, it has been possible to trap the intermediate nitrile ylide with methanol and with other active hydrogen compounds.[10,11] This suggested to us the possibility of devising a new synthesis of cycloalkanones based upon the photolysis of spiroazirines **1a–d**[12] in the presence of alcohol followed by a hydrolysis step (Scheme I). In exploring this synthetic route, we discovered an unusual photochemical cycloelimination of 2-phenyl-1-azaspiro[2.2]pent-1-ene (**1a**) giving the extremely novel carbene, 2-phenylazirinylidene. We wish to report herein evidence concerning the formation and reactions of this species.

Scheme I



Irradiation of spiroazirines **1b–d** in methanol, or in pentane containing excess methanol, resulted in the quantitative formation of imines **3b–d**.[13] Clean conversion to benzaldehyde and the corresponding cycloalkanone **4** was accomplished by treating the photoproduct with a 10% aqueous hydrochloric acid solution.

In contrast to the above results, photolysis of spirocyclopropylazirine **1a** under a nitrogen atmosphere in pentane containing excess methanol produced a complex mixture of products. Analysis of the mixture by GLPC and NMR indicated the presence of eight major components, seven of which have been identified on the basis of their spectral properties or by comparison with known compounds.[13] Hy-