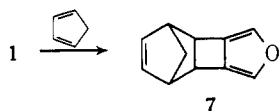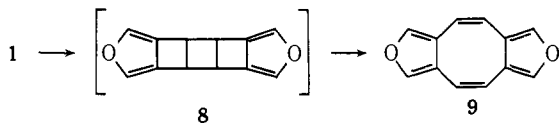showed a parent peak at m/e 92 and base peak at m/e 64 ($M^+ - CO$), and by the fact that when allowed to stand in acetone solution, 1 slowly formed the known[6]


cyclic 16π-bisfurocyclooctatetraene 9, presumably via $2 + 2$ dimer 8.

Compound 1 is of theoretical interest for a number of reasons. It can be viewed as a heterocyclic analog of benzocyclobutadiene (11), which (unlike 1) has been

generated only in transient form.[7] Of major concern also is its stability compared with that of furan (12) and oxepin (13). Thermodynamic data on 1 will be difficult to obtain; clearly, however, it is reluctantly
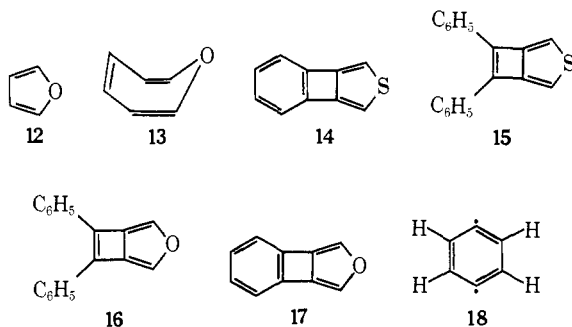
formed (despite the often similar thermal reactivity of oxiranes and cyclopropanes,[8] 4 is converted to 1 much less readily than 5 goes to 6) and more reactive[9] than either 12 or 13. This is undoubtedly partially due to a high strain energy, but its sensitivity compared even to triene 6 suggests that its apparent instability has a substantial electronic component as well. The nmr spectrum of 1 is ambiguous with regard to the presence of a ring current; clearly the paramagnetic component[10]

in 1 (α-hydrogen chemical shift at δ 6.28 ppm) is much greater than that in furan (α-hydrogen chemical shift at δ 7.40 ppm), but whether one should consider 1 to be "nonaromatic" or "antiaromatic" on the basis of ring current effects is still open to question[11] (e.g., compare[9] α hydrogens in 13, δ 5.7; 7, 6.72; 9, 7.27 ppm). In any case, both the four- and five-ring protons appear at relatively high field, indicating the absence of a large polarization of charge in 1.

Compounds 14 and 15, which are substituted analogs of 1, are considerably less reactive substances.[12,13] Attempts to prepare oxygen analogs 16 and 17 have failed,[14] undoubtedly because their sensitivity approaches that of 1. Finally, the contrast between the structures of 1,4-dehydrobenzene (18)[15] and 3,6-dehydrooxepin is striking; apparently these compounds lie on opposite sides of the energetic borderline that determines whether the "dehydro" bond is open,[15] as in 17, or closed, as it is in 1.

(11) Perhaps the term "schizoantiaromatic" would be consistent with an earlier suggestion: cf. E. Heilbronner, as quoted by D. Ginsburg, as quoted by J. F. Stoddart, Chem. Brit., 250, 490 (1971).

(12) P. J. Garratt and K. P. C. Vollhardt, Chem. Commun., 109 (1970).

(13) P. J. Garratt and K. P. C. Vollhardt, J. Amer. Chem. Soc., 94, 1022 (1972).

(14) P. J. Garratt and K. P. C. Vollhardt, private communication.

(15) R. R. Jones and R. G. Bergman, J. Amer. Chem. Soc., 94, 660 (1972).

(16) (a) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher–Scholar, 1970–1975.

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(6) J. A. Elix, M. V. Sargent, and F. Sondheimer, J. Amer. Chem. Soc., 89, 5080 (1967); 92, 973 (1970).

(7) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapter 6.

(8) (a) It is not clear whether one should a priori expect cyclopropanes to have greater or similar thermal reactivity compared with oxiranes. For example, cis-1,2-divinyloxirane rearranges[8b] to 4,5-dihydrooxepin at temperatures below 100° with $E_a = 24.6$ kcal/mol and $\Delta S^{\ddagger} = 0.4$ eu, whereas cis-1,2-divinylcyclopropane rearranges to 1,5-cycloheptadiene so quickly that numerous attempts to isolate it have been unsuccessful.[8c] However, trans-1,2-divinyloxirane and trans-1,2-divinylcyclopropane have very similar reactivities ($E_a = 36$ and 35 kcal/mol, $\Delta S^{\ddagger} = 0.4$ and 2.0 eu, respectively[8b,8c]), suggesting that 4t, at least, may be unusually unreactive since it rearranges so much more slowly than does 5t. (b) E. Vogel and H. Günther, Angew. Chem., Int. Ed. Engl., 6, 385 (1967); (c) S. J. Rhoads, private communication; (d) for related examples, see R. J. Crawford and T. R. Lynch, Can. J. Chem., 46, 1457 (1968); (e) H. H. J. MacDonald and R. J. Crawford, ibid., 50, 428 (1972); (f) L. B. Rodewald and C. H. DePuy, Tetrahedron Lett., 2951 (1964).

(9) E. Vogel, W. A. Böll, and H. Günther, ibid., 609 (1965).

(10) F. Baer, H. Kuhn, and W. Regel, Z. Naturforsch. A, 22, 103 (1967).

Mechanism of the Photochemical Transformation of a 1,3,5-Hexatriene to a Bicyclo[3.1.0]hex-2-ene[1]

Sir:

The photoinduced rearrangement of conjugated 1,3,5-trienes to bicyclo[3.1.0]hex-2-ene ring systems has been the focus of much research[2] since the process was first reported in 1958.[3] This two-bond forming reaction has been looked upon as a photochemical Diels–Alder reaction and has been designated as a concerted [$_\pi 4 + _\pi 2$] cycloaddition.[4] While data have been presented that appear to substantiate the proposed concerted nature of the rearrangement,[2,5] other recent studies have indicated that a related reaction process may in fact proceed via a nonconcerted

(1) This work was supported in part by the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Grant No. AM-00709.

(2) A. Padwa and S. Clough, J. Amer. Chem. Soc., 90, 5803 (1970), and references cited therein.

(3) W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, Jr., and H. Urscheler, ibid., 80, 4116 (1958); W. G. Dauben and P. Baumann, Tetrahedron Lett., 565 (1961).
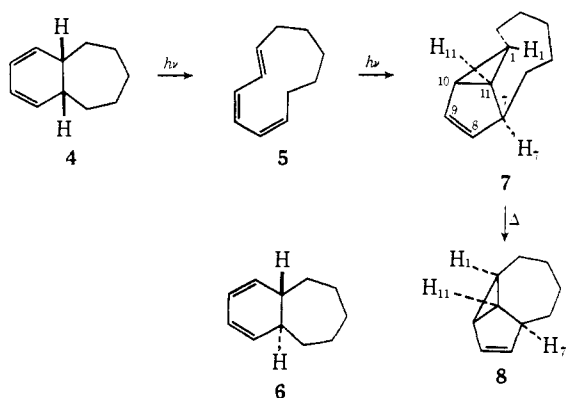
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(5) A. Padwa, L. Brodsky, and S. Clough, Chem. Commun., 417 (1971).

route.[6] Furthermore, other workers have suggested that the rearrangement occurs specifically from the s-trans–s-cis conformation,[7,8] the s-cis–s-cis conformation leading to a cyclohexadiene.[7,9]
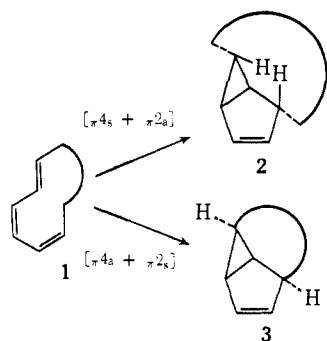
The general orbital symmetry evaluation of a concerted $[_\pi4 + _\pi2]$ cycloaddition[4,10] which treats the triene system as two independent basis sets, i.e., diene and olefin, predicts equal allowedness for a $[_\pi4_s + _\pi2_a]$ and a $[_\pi4_a + _\pi2_s]$ process. However, if the nodal symmetry of the triene lowest unoccupied molecular orbital [LUMO] and the preference for an s-trans–s-cis conformation are considered, only the $[_\pi4_s + _\pi2_a]$ process would be allowed. In order to test this latter restriction, a conjugated triene of type 1 was studied in which the LUMO allowed $[_\pi4_s + _\pi2_a]$ process for the required conformation would lead to a sterically highly strained exo,exo product 2 but the $[_\pi4_a + _\pi2_s]$ mode would lead to lesser strained endo,endo compound 3.[11]

Irradiation of cis-bicyclo[5.4.0]undeca-8,10-diene (4)[12] in pentane with a 450-W Hanovia mercury lamp through Corex (λ >235 nm) resulted in efficient formation of cis,cis,trans-1,3,5-cycloundecatriene (5) which was isolated by preparative vpc[13] or by chromatography on alumina impregnated with 25% silver nitrate.

At conversions up to 50%, 5 was the only product detected that underwent further photoisomerization; no trans,cis,trans-1,3,5-cycloundecatriene was found. Important spectral features of 5 were: ir (CCl$_4$) 980 cm^{-1}; nmr δ (CCl$_4$) 6.2–5.1 (m, 6), 2.3–1.9 (m, 4), 1.5 (m, 6); uv max (hexane) 254 nm (ϵ 5000); mass spectrum m/e 148. When 5 was heated in a sealed tube in hexane at 150° for ·1 hr, it rearranged, quantitatively, to the trans-diene 6 which displayed the following spectral properties: ir (CCl$_4$) 690 cm^{-1}; nmr δ (CCl$_4$) 5.53 (q, 4, $\delta_A - \delta_B = 0.25$ ppm, $J_{AB} = J_{A'B'} = 10$ Hz), 2.17 (m, 2), 1.62 (m, 10); uv max (hexane) 264 nm (ϵ 2500). This stereospecific thermal conversion of 5 firmly established its stereochemistry as cis,cis,trans.[4]

Extended irradiation of diene 4 gave rise to one major product (7) in about 30% vpc yield, accounting for about 85% of the volatile products. Isolation of photoisomer 7 by preparative vpc[13] or by silver nitrate chromatography yielded a colorless liquid: mass spectrum m/e 148; ir (CCl$_4$) 1570, 690 cm^{-1}; nmr δ (CCl$_4$) 5.83 (m, 1, vinyl H), 5.26 (m, 1, vinyl H), 3.04 (m, 1, allylic H$_7$), 1.90 (m, 6), 1.10 (m, 6), 0.48 (m, 1, cyclopropyl H$_1$). The signal at δ 3.04 (H$_7$) appears as a doublet of a doublet of doublets, resembling a quartet; analysis of the complex band gives $J_{7,11}$ as approximately 7 Hz. Such a multiplicity is reasonable only if H$_7$ and H$_{11}$ are in a cis arrangment.[2,14] The high-field resonance at δ 0.48 for the cyclopropyl proton is due to shielding by the double bond; thus, an endo configuration of H$_1$ is required. These data indicate photoproduct 7 is 1-exo-7-endo-tricyclo[5.3.-1.0^{10,11}]undec-8-ene.

The photoproduct 7 was thermally stable at 200° (sealed tube in hexane) but at 250° it rearranged (half-life ~40 min). The pyrolysis product was isolated by preparative vpc:[13] mass spectrum m/e 148; nmr δ (CCl$_4$) 5.47 (m, 2), 3.22 (m, 1), 1.55 (m, 13). These spectral data and the thermal stability indicate the pyrolysis product is 1-endo-7-endo-tricyclo[5.3.1.0^{1,10}]-dec-8-ene (8). The presence of a double bond in a five-membered ring in 8 was shown by the formation of a five-membered ring ketone (ir 1740 cm^{-1}) by hydroboration and Collin's oxidation.[15]

The observed exo,endo photoproduct cannot be the result either of a $[_\pi4_s + _\pi2_a]$ or of a $[_\pi4_a + _\pi2_s]$ route starting with the cis,cis,trans-triene 5. Such a product could be the result of the isomeric trans,cis,-trans isomer. Monitoring the product composition at low conversion showed that the bicyclo[3.1.0]-hexene 7 was formed early in the reaction and if it came from the trans,cis,trans-triene, this isomer would need to be formed in a highly efficient manner. Such was not the case since triene 5 was found to be 20% of the reaction mixture at 50% conversion.

The formation of the exo,endo product 7 can be rationalized when it is recognized that a bicyclo[3.1.0]-hexene is actually a vinylogous bicyclo[1.1.0]butane. The formation of this latter type of product from an s-trans-diene has been shown to proceed via an initial conrotatory closure of a twisted allylmethylene relaxed singlet excited state.[16] The electronically excited but

(6) D. A. Seeley, J. Amer. Chem. Soc., 94, 4378 (1972).

(7) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, ibid., 94, 4285 (1972).

(8) P. J. Vroegop, Dissertation, Leiden, 1972. We thank Professor E. Havinga and Dr. J. Lugtenburg for a copy of this thesis.

(9) W. G. Dauben and M. S. Kellogg, J. Amer. Chem. Soc., 93, 3805 (1971).

(10) H. E. Zimmerman, Accounts Chem. Res., 4, 272 (1971); M. J. S. Dewar, Angew. Chem., Int. Ed. Engl., 10, 761 (1971).

(11) Formation of the endo,endo product is LUMO allowed from the s-cis–s-cis conformation. However, it is unlikely that a $[_\pi4_a + _\pi2_s]$ process would occur from this conformation.[7]

(12) J. Monthony, Ph.D. Dissertation, University of California, Riverside, 1971.

(13) Preparative vpc was conducted on a 6 ft × ¼ in., 5% Carbowax 20 M, 5% KOH on 60–80 Chromosorb G column at 120°.

(14) H. Heimgartner, L. Ulrich, H. J. Hansen, and H. Schmid, Helv. Chim. Acta, 54, 2313 (1971).

(15) J. C. Collins, W. W. Hess, and F. J. Frank, Tetrahedron Lett., 3363 (1968).

vibrationally relaxed triene may also have a configuration where the central double bond has twisted, *i.e.*, a bisallyl excited state.[17] The present results suggest that the formation of a bicyclo[3.1.0]hexene proceeds
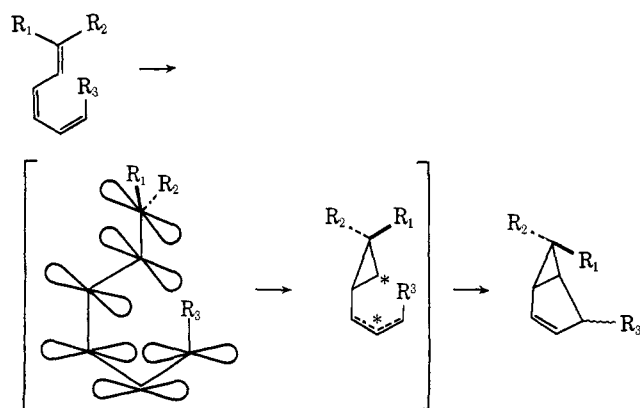
from this relaxed state by the allowed conrotatory closure to the cyclopropane ring followed by closure of the five-membered ring. This mechanism accounts for the required involvement[7,8] of an s-cis-s-trans conformation in the formation of a bicyclo[3.1.0]-hexene, for the high specificity[3,18] for conrotatory closure in the formation of the cyclopropane moiety at the end of the molecule most likely to exist in the s-trans arrangement, and for the stereospecificity observed in cyclopropane ring formation but lack of it in the closure of the five-membered ring where the isomer with the more stable configuration is formed.[2,6,14]

(16) W. G. Dauben and J. S. Ritscher, *J. Amer. Chem. Soc.*, 92, 2925 (1970).

(17) R. S. H. Liu and Y. Butt, *ibid.*, 93, 1532 (1971).

(18) J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, 87, 3532 (1965); J. Meinwald and P. H. Mazzocchi, *ibid.*, 88, 2850 (1966).

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Regioselectivity and Reactivity in the 1,3-Dipolar Cycloadditions of Diazonium Betaines (Diazoalkanes, Azides, and Nitrous Oxide)

Sir:

Although experimental investigations of 1,3-dipolar cycloadditions have established the concerted mechanisms of these reactions,[1] the origin of regioselectivity in 1,3-dipolar cycloadditions has remained the greatest unsolved problem in this area of chemistry.[2,3] This communication, which provides a complete rationalization of the regioselectivity of diazonium betaine cycloadditions, along with the recent work of Sust-

(1) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 565, 633 (1963); R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 739; R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, 105, 1324 (1972), and earlier papers in this series.

(2) (a) R. A. Firestone, *J. Org. Chem.*, 33, 2285 (1968); (b) R. Huisgen, *ibid.*, 33, 2291 (1968); (c) R. A. Firestone, *J. Chem. Soc. A*, 1570 (1970); (d) R. A. Firestone, *J. Org. Chem.*, 37, 2181 (1972).

(3) Ch. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer-Verlag, Heidelberg, 1971, p 95.

mann,[4,5] demonstrates that for one important class of 1,3 dipoles, a perturbation model for the concerted mechanism accounts both for reactivity patterns and for the regioselectivity of these reactions.

In the early stages of a cycloaddition reaction, when the interaction between two addends is small, perturbation theory should give a reliable guide to the most stable geometry of approach of addends, and thus to the preferred regioisomeric transition state.[4-13] Perturbation theory has been used in varying levels of sophistication, from those in which σ, π, and Coulombic interactions are evaluated,[10,11] to those in which only the "frontier" π orbitals of the two addends are considered.[6,9] The latter approach, which should be reliable as long as steric and electrostatic interactions are similar for diastereomeric transition states, is applied here to 1,3-dipolar cycloaddition regioselectivity.

The interaction of an occupied orbital on one addend with an unoccupied orbital on the other addend results in a stabilization which is (1) inversely proportional to the difference in energy between the interacting orbitals, and (2) directly proportional to the square of the sum of the products of coefficients of interacting centers.[6-9] The first conclusion suggests that frontier orbital interactions should provide the predominant electronic stabilization of a transition state, while the second implies that of two regioisomeric adducts, that one will be favored in which the largest coefficients on the HO and LU of the two addends are united.[13]

Through qualitative perturbation theory and a correlation of the relative rates of phenyl azide–dipolarophile reactions with the dipolarophile ionization potentials, Sustmann has shown that (1) for electron-deficient[14] alkenes, the difference between azide HO and dipolarophile LU energies determines reactivity, (2) for electron-rich alkenes, the difference between azide LU and dipolarophile HO energies determines reactivity, and (3) for conjugated dipolarophiles, both HO–LU energy differences are important.[4,5] The following considerations show that the same interactions determine the regioselectivity of 1,3-dipolar cycloadditions.

The HO and LU π molecular orbitals of hydrazoic acid calculated by the CNDO/2 method are shown in Figure 1b.[15,16] These orbitals are similar to those of

(4) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).

(5) R. Sustmann and H. Trill, *Angew. Chem., Int. Ed. Engl.*, 11, 838 (1972). The author thanks Dr. Sustmann for a preprint of this paper.

(6) W. C. Herndon, *Chem. Rev.*, 72, 157 (1972).

(7) L. Salem, *J. Amer. Chem. Soc.*, 90, 543, 553 (1968).

(8) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(9) K. Fukui, *Fortschr. Chem. Forsch.*, 15, 1 (1970).

(10) R. Sustmann and G. Binsch, *Mol. Phys.*, 20, 1, 9 (1971).

(11) A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, 91, 3793 (1969); A. Devaquet, *Mol. Phys.*, 18, 233 (1970).

(12) T. Inukai, H. Sato, and T. Kojima, *Bull. Chem. Soc. Jap.*, 45, 891 (1972); see also J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, 24, 2575 (1968).

(13) O. Eisenstein, J.-M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971).

(14) "Electron-deficient" alkenes are simultaneously conjugated alkenes, so that the designation is somewhat arbitrary.

(15) The shaded areas represent positive lobes, and the relative orbital sizes schematically represent magnitudes of $2p_z$ coefficients. For example, the CNDO/2 calculation for $HN_1N_2N_3$ gives the following eigenvectors: $\pi_{HO} = 0.807(2p_z)_1 + 0.014(2p_z)_2 - 0.591(2p_z)_3$; $\pi_{LU} = -0.426(2p_z)_1 + 0.708(2p_z)_2 - 0.564(2p_z)_3$. The relative magnitudes of coefficients remain the same for hydrazoic acid and alkyl and aryl azides in both EHT and CNDO/2 calculations. Similar results have been obtained for a variety of 1,3 dipoles.[16]