V. Ya. Bykhovsky, N. J. Zaitseva, and V. N. Bukin, *Tetrahedron Lett.*, 2217 (1977).
(8) A. R. Battersby, E. McDonald, M. Thompson, and V. Ya. Bykhovsky, *J. Chem. Soc., Chem. Commun.*, 150 (1978).
(9) L. M. Siegel, M. J. Murphy, and H. Kamin, *J. Biol. Chem.*, **248**, 151 (1973); M. J. Murphy and L. M. Siegel, *ibid.*, **248**, 6911 (1973).
(10) Factor I has recently been shown to have structure **4**. G. Müller, R. Deeg, K. D. Gneuss, G. Gunzer, and H.-P. Kriemler, *Proc. Eur. Symp. Vitamin* B_{12}, *3rd, 1979*, in press.
(11) A. R. Battersby and E. McDonald, *Bioorg. Chem.*, **7**, 161 (1978).
(12) Unpublished work by Drs. D. Schneider, M. M. Schneider, and S. Hosozawa.
(13) In earlier experiments it was clearly shown[1a,14] that, under carefully controlled conditions, [^{14}C]formaldehyde could be trapped from the C-20 position of uro'gen III. The data can be interpreted in several ways: (a) methylation at C-20 is followed by loss of a "C_2" unit which is further cleaved to "C_1" units, one of which is trapped as formaldehyde; (b) the formaldehyde is released (under enzymic control[15]) *only* from the uro'gen III molecule and *not* from factor III; (c) more than one pathway exists for the biotransformation of uro'gen III to cobyrinic acid.
(14) M. Kajiwara, K. S. Ho, H. Klein, A. I. Scott, A. Gossauer, J. Engel, E. Neumann, and H. Zilch, *Bioorg. Chem.*, **6**, 397 (1977).
(15) This interpretation would entail the fortuitous correspondence of the stoichiometry of formaldehyde release (3%) from ^{14}C-20 and bioconversion of the ^{14}C-5 and ^{14}C-15 labels in uro'gen III to these positions in cobyrinic acid (~3%).[14]

G. Müller,* K. D. Gneuss
Institut für Organische Chemie
Biochemie und Isotopenforschung
Universität Stuttgart, Pfaffenwaldring 55
D-7000 Stuttgart 1, Germany

H.-P. Kriemler
Z-F.F., Ciba-Geigy AG, CH-4002 Basel, Switzerland

A. I. Scott,* A. J. Irwin
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received March 26, 1979

Planar *s-cis*-1,3-Butadiene

Sir:

It has long been recognized that 1,3-butadiene exists in two conformations.[1] A number of calculations and experiments on this compound have been reported,[2] and the geometry of the more stable rotamer has been shown to be planar s-trans.[3] Both planar and twisted (gauche) geometries have been proposed for *s-cis*-1,3-butadiene, but the actual geometry has not been established. The energy barrier separating *s-cis-* from *s-trans*-1,3-butadiene and the relative energies of these two compounds are in question. We wish to describe the preparation of *s-cis*-1,3-butadiene by thermal trapping and photochemical generation, the spectroscopic (IR and UV) characterization of this molecule, and a direct measurement of the barrier separating *s-cis-* from *s-trans*-1,3-butadiene.

We have previously shown that it is possible to thermally generate and trap at low temperature a mixture of conformers rich in higher energy forms.[4] When 1,3-butadiene is passed as a vapor through a hot tube (400–900 °C) and allowed to impinge on a CsI plate cooled to 30 K, infrared bands can be observed which are not present in a spectrum of 1,3-butadiene deposited from room temperature.[5] When the CsI window is warmed to 60 K, these new bands rapidly disappear, the bands corresponding to s-trans increase, and the remaining spectrum is identical with that of a sample deposited from room temperature. On the basis of this rapid conversion to *s-trans*-1,3-butadiene, the additional bands[6] in the high-temperature deposition can be assigned to the s-cis conformer.

A 1,3-butadiene/argon mixture (1:1000) was also deposited from high temperatures (400–900 °C) onto a CsI window cooled to 20 K (Figure 1). Bands were again observed which were not present in the infrared spectrum obtained of this mixture deposited from room temperature.[7] These bands[8] correspond well to those found in the spectra derived from neat high-temperature depositions. The additional bands produced in the high-temperature depositions are, therefore, due to the s-cis conformer rather than to any crystalline effects. Broadband irradiation of the conformer mixture matrix isolated in argon, using a 1000-W high-pressure mercury-xenon lamp with quartz optics, resulted in the rapid disappearance of the s-cis infrared bands with a concomitant increase in the intensity of the *s-trans*-1,3-butadiene bands.[9] Prolonged irradiation of the matrix containing *s-trans*-1,3-butadiene slowly produced vinylacetylene. Neither cyclobutene nor bicyclobutane was observed.[10]

The UV spectrum of the high-temperature conformational mixture of 1,3-butadiene matrix isolated (1:2000) in argon at

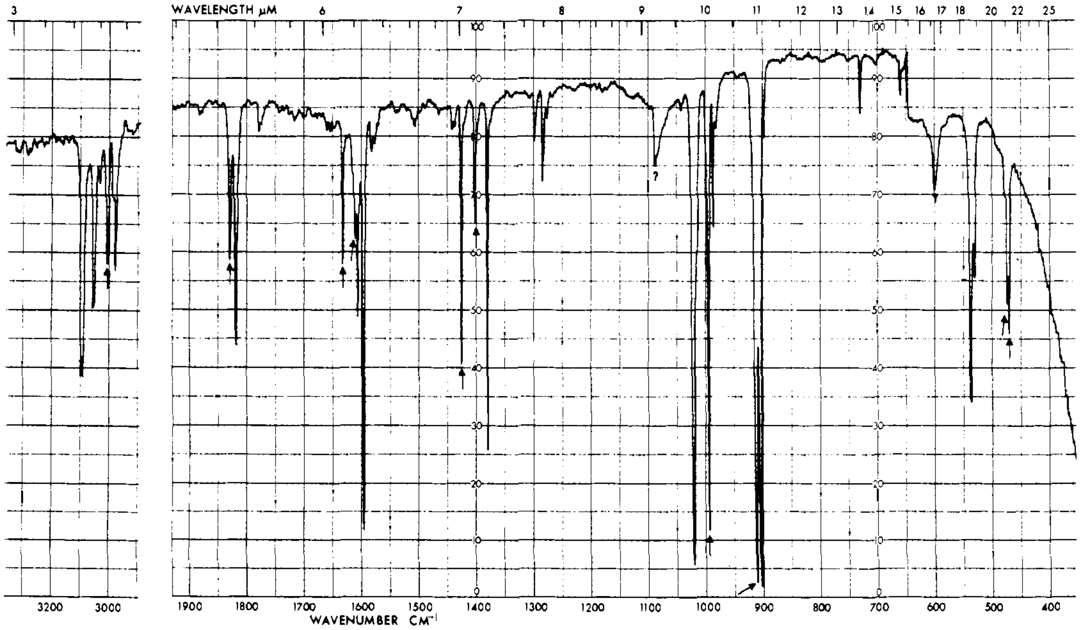


Figure 1. Infrared spectrum between 3400 and 2900 cm^{-1} and between 1930 and 350 cm^{-1} at 20 K of matrix-isolated 1,3-butadiene (1:700 in argon) deposited from 850 °C. The arrows designate bands assigned to the s-cis form. The bands at 1089 and 600 cm^{-1} are rather broad, but these bands are probably also due to *s-cis*-1,3-butadiene.

0002-7863/79/1501-3657$01.00/0

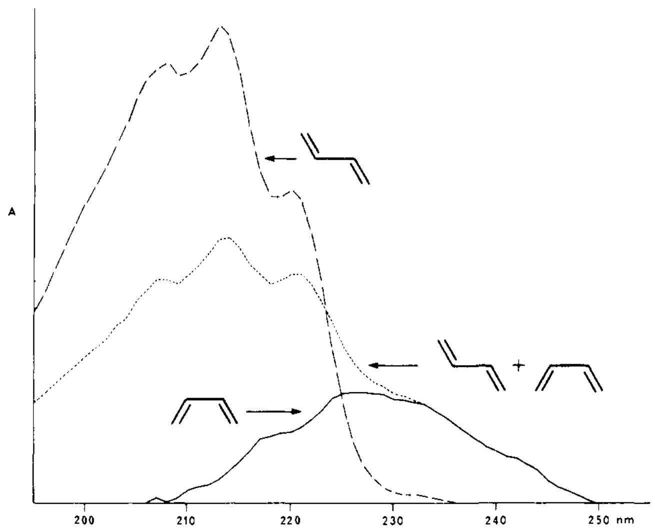


Figure 2. Ultraviolet spectra of 1,3-butadiene matrix isolated in argon (1:2000) at 20 K: A, (. . .) spectrum taken after 120-min irradiation at 214 nm; B, (- - -) same sample after 0.5-min irradiation ($\lambda > 200$ nm) with Hg-Xe lamp; (C, —) spectrum of *s-cis*-1,3-butadiene obtained from the data in (A) and (B) on the assumption that only the s-trans form absorbs at about 200 nm. All spectra are corrected for baseline absorption.

20 K showed an absorption which appeared as a shoulder on the long-wavelength side of the s-trans absorption (λ_{max} 212 nm). Brief irradiation of the matrix (mercury-xenon lamp) caused the disappearance of the shoulder and a simultaneous increase in the s-trans absorption. This shoulder was not evident in the UV spectrum of 1,3-butadiene deposited from room temperature. These results indicate that the shoulder corresponds to the photochemically labile species observed in the analogous infrared experiment, and hence represents the UV absorption of *s-cis*-1,3-butadiene. A high-pressure mercury-xenon lamp has a precipitous decrease in light intensity below 230 nm.[11] The s-cis conformer thus absorbs more light above 230 nm (see Figure 2), and the photostationary state favors the s-trans isomer. Irradiation of argon matrix isolated *s-trans*-1,3-butadiene (1:2000) with a zinc spectral lamp, which has a strong emission at 214 nm,[12] led to a dramatic decrease of the s-trans UV absorption and the appearance of a strong absorption due to the s-cis isomer. Subsequent irradiation with the mercury-xenon lamp gave back the original spectrum although with a slight decrease in intensity.[13] Deconvolution of the spectrum of the photoinduced conformational mixture gave the UV spectrum of the high-energy conformer, which shows a 226-nm maximum[14] (Figure 2). The presence of an isosbestic point in the photochemical conversion of the s-cis to the s-trans isomer allows the value of 0.45 to be calculated for the ratio of the extinction coefficients $\epsilon_{s\text{-cis}}/\epsilon_{s\text{-trans}}$, at the maxima of the absorbances of the two isomers. If the solution phase ϵ of the s-trans conformer (20 900)[15] compares with the ϵ of the matrix-isolated species, then the extinction coefficient at the 226-nm λ_{max} of *s-cis*-1,3-butadiene is 9400.

Ab initio[16] and Pariser-Parr π-electron calculations[17] predict that a gauche (nonplanar) geometry will exhibit a UV maximum higher or equal in energy to that of the planar s-trans conformer. A planar s-cis conformer is expected to have a UV maximum 8 to 20 nm longer in wavelength than the s-trans form. These predictions are consistent with the UV spectra of cyclic cisoid dienes with constrained geometries.[17] The 226-nm maximum implies that the s-cis conformer of 1,3-butadiene is planar.[18] The UV data are strongly against a gauche geometry having a significant twist angle. A small twist angle (say, <15°) would fit the data, but the energy difference between 0° and ±15° would then be expected to be so small that the zero-point torsional level would probably lie above the potential energy for the planar geometry, making a strictly geometric distinction almost meaningless. Furthermore, the low temperature at which the spectra are obtained (20 K) assures that the absorption centered at 226 nm originates from the lowest torsional level and therefore reflects the zero-point torsional geometry of *s-cis*-1,3-butadiene.

Kinetic analysis of the thermal conversion of *s-cis*- to *s-trans*-1,3-butadiene (trapped neat from 800 °C) permitted determination of the s-cis to s-trans energy barrier. Rates of decay of *s-cis*-1,3-butadiene were measured using the infrared band at 1430 cm^{-1}.[21] From these rates a free energy of activation ($\approx\Delta H^{\ne}$) of 3.9 ± 0.2 kcal/mol can be calculated for the s-cis to s-trans process, using the absolute rate equation from transition state theory.[22] This value can be compared with experimental results obtained from an analysis of the Raman overtones of the torsional vibration by Carreira (4.7 kcal/mol)[2c] and Durig et al. (4.3 kcal/mol).[19] Force field calculations by Allinger and Tai[2f] predict an energy barrier of 4.7 kcal/mol for this process.

A good picture of the ground-state energy surface of the 1,3-butadiene molecule thus emerges. The minor form has been shown to have a planar or very nearly planar (<15°) s-cis geometry, and the activation barrier for the s-cis to s-trans conversion, 3.9 kcal/mol, has been measured. The energy diffence between these two species is not certain, although the best estimates fall in the range 2.5–3.1 kcal/mol.[2,19] Further work on the low-temperature photochemistry of this and other 1,3-dienes will be reported in a later paper.

Acknowledgments. This research was supported by Grant GM-24427 from the Institute of General Medical Sciences, U.S. Department of Health, Education, and Welfare, and Grants CH75-10939 and CHE76-01788 from the National Science Foundation. The authors wish to thank Professors J. Michl and J. Joussot-Dubien for helpful discussions.

References and Notes

(1) E. Hückel, *Z. Phys.*, **76**, 630 (1932).

(2) (a) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) R. L. Lipnick and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **95**, 6370 (1973); (c) L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975); (d) D. Compton, W. O. George and W. F. Maddans, *J. Chem. Soc., Perkin Trans. 2*, 1666 (1976); (e) S. Shih, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **16**, 244 (1972); (f) J. C. Tai and N. L. Allinger, *J. Am. Chem. Soc.*, **98**, 7928 (1976).

(3) (a) A. Almenningen and M. Traetteburg, *Acta Chem. Scand.*, **12**, 1221 (1958); (b) W. Haugen and M. Traetteburg, "Selected Topics in Structural Chemistry", Universitetsforlaget, Oslo, Norway, 1967; (c) K. Kuchitsu, T. Fukyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).

(4) (a) F. A. L. Anet and M. Squillacote, *J. Am. Chem. Soc.*, **97**, 3243 (1975); (b) M. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *ibid.*, **97**, 3244 (1975).

(5) Bondybey and Nibler have suggested that some bands which are the result of a deposition of 1,3-butadiene onto a cooled window might derive from an s-cis form: V. E. Bondybey and J. W. Nibler, *Spectrochim. Acta, Part A*, **29**, 645 (1973).

(6) The infrared bands assigned to *s-cis*-1,3-butadiene deposited neat from high temperature are at 1640 (0.11), 1632 (0.27), 1608 (0.13), 1440 (0.13), 1429 (0.66), 1403 (0.24), 1200 (0.06), 1005 (1.00), 760 (0.06), 740 (0.10), 600 (0.09), 510 (0.09), and 480 (0.20) cm^{-1}. Relative intensities are given in parentheses.

(7) Huber-Wälchli has obtained matrix-isolated spectra of *s-cis*-1,3-butadiene using a technique similar to ours. He also reports an s-cis–s-trans energy difference of 2.5 ± 0.5 kcal/mol. The details leading to this value, however, were not given: P. Huber-Wälchli, *Ber. Bunsenges Phys. Chem.*, **82**, 10 (1978).

(8) The infrared bands assigned to *s-cis*-1,3-butadiene matrix isolated in argon are at 3020 (0.24), 1828 (0.30), 1632 (0.31), 1612 (0.25), 1425 (0.50), 1402 (0.23), 1089 (0.13), 995 (0.86), 913 (1.00), 600 (0.16), 475 (0.29), and 472 (0.35) cm^{-1}. Relative intensities are given in parentheses.

(9) This increase should be a measure of the amount of the s-cis conformer originally trapped. However, site splitting led to unreliable intensities and therefore to large errors in the $\Delta H°$ (4 ± 1 kcal/mol) and $\Delta S°$ (2 ± 1 eu) values determined from data obtained with different oven temperatures. Use of the van't Hoff equation on absorbance ratios of trapped conformational mixtures also gave rather large errors for $\Delta H°$.

(10) The absence of these products may be explained by the presence of energy barriers in the excited state manifold: (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969); (b) D. Grimbert, G. Segal, and A. Devaquet, *ibid.*, **97**, 6629 (1975).

(11) Oriel Corporation of America Catalog, 1975, p 75.

(12) H. Habeeb, D. U. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.*, **10**, 251 (1942).

(13) This decrease is due to the production of some vinylacetylene during the irradiation of 1,3-butadiene with the Zn lamp.

(14) Irradiation (214 nm) of the significantly thicker matrix necessary for the infrared experiments produced a small amount of *s-cis*-1,3-butadiene and vinylacetylene (by IR). Internal filtering by the s-cis isomer (which has some absorption at 214 nm) produced near the surface of the matrix, however, prevented the establishment of a photostationary state throughout the entire sample.

(15) "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds", J. G. Brasselli, Ed., CRC Press, Cleveland, Ohio, 1973.

(16) (a) B. Dumbacher, *Theor. Chim. Acta.*, **23,** 346 (1972); (b) A. Devaquet, R. E. Townsend, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 4068 (1976).

(17) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86;** 2811 (1964).

(18) Previous experimental evidence which was considered to support a gauche geometry for *s-cis*-1,3-butadiene[2b,19,20] can be interpreted equally well on the basis of a planar geometry. Lipnick and Garbisch[2b] analyzed the temperature dependence of the NMR parameters in 1,3-butadiene and claimed that the entropy required to fit the data favored a gauche geometry for the s-cis form. Unfortunately, these workers treated the errors assigned to various parameters as being independent of one another, whereas they are, in fact, highly correlated, and this results in the true error limits of ΔS° being so large that a geometric assignment can no longer be made.

(19) J. R. Durig, W. E. Buey, and A. R. H. Cole, *Can. J. Phys.*, **53,** 1832 (1976).

(20) V. I. Tyulin, *Zh. Strukt. Khim.*, **15,** 639 (1974).

(21) Rate constants of 9×10^{-5}, 5×10^{-4}, and 2×10^{-4} s^{-1} were measured at 53, 55, and 56 K respectively. The error reported is 2 std of the $\Delta G^\ddagger$ values obtained from the three rates of decay.

(22) S. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p 250.

(23) National Science Foundation Predoctoral Fellow, 1974–1977.

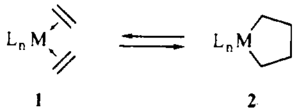
M. E. Squillacote, R. S. Sheridan,[23]
O. L. Chapman,* F. A. L. Anet*
Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received January 24, 1979

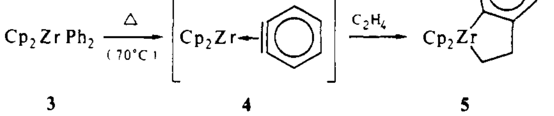
Equilibrium between Metallaindans and Aryne Olefin–Metal Complexes[1]

Sir:

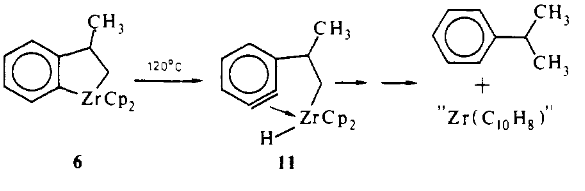
The equilibrium between bis(olefin)-transition metal complexes **1** and metallacyclopentanes **2** appears to be an important step in many catalytic reaction sequencies[2] (eq 1). This transformation has been observed with a variety of transition metals, and it has been suggested as being a quite general reaction.[3] More detailed information about this important structural relation is, however, scarce. Most of the data available has been obtained from studies on the parent systems, the unsubstituted metallacyclopentanes.[4] There is, however, very little known about how sensitive this rearrangement is to variations in the organic moieties of the complexes.



1 **2** (1)



3 **4** **5** (2)



6 **11** (3)

Table I. Thermolysis of Biscyclopentadienylzirconaindans

compd	neat, dec temp, °C[a]	in the presence of olefins: $\Delta G^\ddagger_{80.5\,°C}$, kcal/mol[b]	in the presence of olefins: solvent
5	130	29.9 ± 0.4	1-octene
		30.3 ± 0.4	norbornene
6	120	27.8 ± 0.3	1-octene
7	105	27.6 ± 0.3	isooctane–1-octene
			isooctane–norbornene
8	115	29.4 ± 0.9	norbornene
9	170	31.6 ± 0.8	isooctane–5,5-dimethylnorbornene

[a] Half life of 1 h. [b] For the formation of aryne olefin zirconocenes at 80.5 °C, obtained from the initial slope of the first-order plot. [c] 3,3-Dimethyl-1-[bis(η^5-cyclopentadienyl)zircona]indan.

A severe perturbation of the system would presumably result, if one of the olefinic ligands of **1** could be replaced by dehydrobenzene, because the energy content of the bis(olefin) structure should be increased by this structural change relative to the metallacycle. Moreover, this would hopefully lead to thermally more stable compounds and simpler overall kinetics, since dissociation of the aryne ligand from the complex should be an unfavorable process.[5] Consequently we developed a synthetic route to 1-metallaindans. The reaction of dehydrobenzenezirconocene (**4**, generated from diphenylzirconocene[6]) with ethylene (20 bar) produces a 95% yield of metallaindan **5** (eq 2). Likewise metallaindans regioselectively (≥95%) bearing the substituent in the 3 position are obtained from substituted olefins.[7]

In contrast to most metallacyclopentanes, temperatures above 100 °C are required to start the decomposition of the zirconaindans (Table I). In solution the corresponding phenylalkanes are the only organic compounds obtained. When the zirconaindans **7**-d_4 or **9**-d_4, containing labeled aromatic rings, are thermolyzed in saturated hydrocarbon solution, labeled phenylalkanes are obtained. ^{1}H NMR analysis shows the average presence of only three deuterium atoms. No deuterium can be found in the alkyl substituents. Mass spectroscopic analyses of these phenylalkanes reveal the presence of a mixture of products containing one to five deuterium atoms in a distribution which is almost statistical if it derives from initially pure phenylalkanes-d_3. Equally, thermolyses of unlabeled zirconaindans in benzene-d_6 produce phenylalkanes containing some of the isotope bound to the phenyl groups. Thermolyses of the solvent-free zirconaindans under vacuum (10^{-3} Torr) proceed alike, except with 3-*n*-butylzirconaindan (**7**) which produces 2-phenylhexane accompanied by a low yield (~10%) of 1-hexene.

In the presence of olefins, the thermal reactivity of the zirconaindans appears markedly changed. At temperatures significantly lower than required for the decomposition (vide supra), liberation of alkene from the complex is observed. At the same time formation of a new zirconaindan containing the added olefin takes place (eq 4; see below). Upon thermolysis of 3-*n*-butylzirconaindan (**7**) with excess norbornene (1.1 to 20 molar equiv), **9** is almost exclusively obtained (>98%). Equilibration of **7** with the less reactive olefin 1-octene (1 molar equiv) leads to a nearly equimolar mixture of 3-*n*-hexylzirconaindan (**10**) and the starting material. This ratio is shifted in favor of **10** with an increasing 1-octene concentration (9:1 with 5 molar equiv of 1-octene). The pronounced effect of the olefins on the equilibrium stands in contrast to the influences of the olefins on the reaction rate. The rate of decrease in **7**, obtained at the beginning of the reaction, has been found to be independent both of the structure and of the concentration of the added alkene. All zirconaindans studied show a similar behavior.

These results indicate that the zirconaindans studied are

0002-7863/79/1501-3659$01.00/0