cyclopropyl participation in the thermolysis of azo compounds. They proposed that the orientation of cyclopropyl orbitals might play an important role on the cyclopropyl participation.

The photolysis of **1** and synthesis of monoazo compound **6** will be the subject of a future report.

Acknowledgment. I wish to thank Professors S. Masamune and D. L. Whalen for details of the "basketene" synthesis, Dr. E. Hedaya for communication of his unpublished results, Professor L. J. Winters for allowing me time to work on part of this project during my stay at Drexel, Professor C. P. Lillya for valuable discussions, and BASF for a generous gift of cyclooctatetraene.

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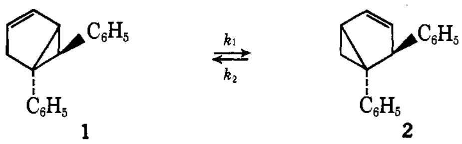
A Stereospecific Vinylcyclopropane Rearrangement Due to Hindered Rotation in the Biradical

Sir:

The thermal reactions of the vinylcyclopropane moiety have attracted considerable interest in recent years. The thermolysis of acyclic vinylcyclopropanes usually leads to cyclopentenes,[1] while the thermal reactions of bicyclo[3.1.0]hex-2-enes results in production of rearranged bicyclo[3.1.0]hex-2-ene(s).[2] In connection with other studies[3] we noted the facile thermal interconversion of *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**1**) and *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (**2**). Since these transformations preserved the stereochemical integrity of the phenyl groups in a formally nonconcerted process,[4] we have studied in some detail the thermal chemistry of **1** and the cis isomer **3**.



Thermolysis of *trans*-**1** in cyclohexane at either 130 or 170° yielded a nearly temperature-invariant mixture of 60% **1** and 40% **2** (Table I). Less than 2% of the corresponding cis isomers, **3** and **4**, could be detected in the time necessary for the **1**:**2** equilibrium to be established.

Table I. Temperature Dependence of the **1** and **2** Equilibrium[a]

Temp, °C	Starting material	Time, hr	% **1**	% **2**
130	**1**	46	59.6	40.4
130	**2**	24	59.2	40.8
170	**1**	2	59.4	40.6
170	**2**	2	58.4	41.6

[a] All products from the thermolyses were isolated by preparative vpc or tlc chromatography. Spectroscopic comparison of the isolated material with authentic samples confirmed the homogeneity and structure of the compounds.

The kinetics of the reaction were determined using a standard ampoule technique with the analysis for **1** and **2** being accomplished by vpc. The rates were calculated assuming a reversible first-order reaction, $(k_1 + k_2)t = \ln [\mathbf{1}_0 - \mathbf{1}_{\text{equil}}]/[\mathbf{1} - \mathbf{1}_{\text{equil}}]$. The reaction gave linear plots of $\ln [\mathbf{1}_0 - \mathbf{1}_{\text{equil}}]/[\mathbf{1} - \mathbf{1}_{\text{equil}}]$ *vs.* t up to the equilibrium mixture of **1** and **2** yielding $k_1 = 10^{12.6}e^{-32.4/RT}$ sec^{-1}.[5]

In contrast to the facile rearrangement of the trans compound, **1**, the corresponding cis isomer, **3**, rearranged slower and yielded besides unreacted **3** (40%), **4** (7%), **1** (32%), and **2** (21%). The rate constants for the thermolysis of **3** were obtained from the concentration *vs.* time curves by the method of Winstein, Young, and Goering[6] and yielded the following rate expression, $k_3 = 10^{13.1}e^{-36.7/RT}$.[7]

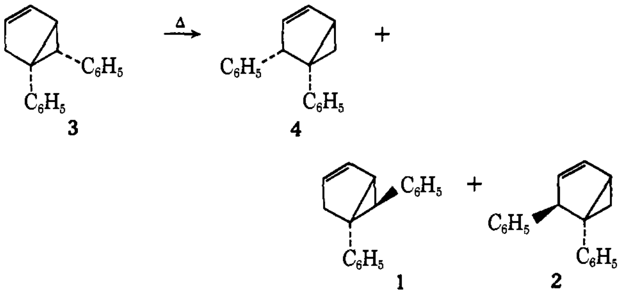


Table II. Rate of Thermolysis of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-ene in Cyclohexane[a]

Temp, °C	Compd	Rate (× 10⁵ sec⁻¹)[b]	ΔE_{act}, kcal/mol
180.0	**1**	94.0	
162.0	**1**	27.0	32.4
144.0	**1**	3.9	
212.0	**3**	39.8	
194.0	**3**	9.11	36.7
180.0	**3**	2.56	

[a] See Table I, footnote *a*. [b] Vpc analysis was performed on a 5 ft × 1/8 in. 5% SE-30 on 100–120 mesh Varaport 30 at 135–145°. In order to obtain good precision the instrument had to be calibrated with known mixtures immediately prior to or following analysis.

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(1) (a) C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.*, **82**, 1007, 4891 (1960); (b) E. Vogel, *Angew. Chem.*, **72**, 4 (1960), ref 162; (c) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (d) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); (e) H. M. Frey and D. C. Marshall, *ibid.*, **58**, 3981 (1962); (f) R. J. Ellis and H. M. Frey, *ibid.*, **60**, 4188 (1964); (g) C. S. Elliott and H. M. Frey, *ibid.*, **61**, 345 (1965); (h) H. M. Frey and A. Krantz, *J. Chem. Soc. A*, 1159 (1969); (i) R. M. Willcott and W. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4310 (1969); (j) P. H. Mazzochi and H. J. Tamburin, *ibid.*, **92**, 7221 (1970).

(2) (a) W. E. von Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963); (b) J. N. Lowe, *Diss. Abstr.*, **25**, 840 (1964); (c) R. H. Eastman, Final Technical Report, AFOSR Contract No. AF-49-638-1272.

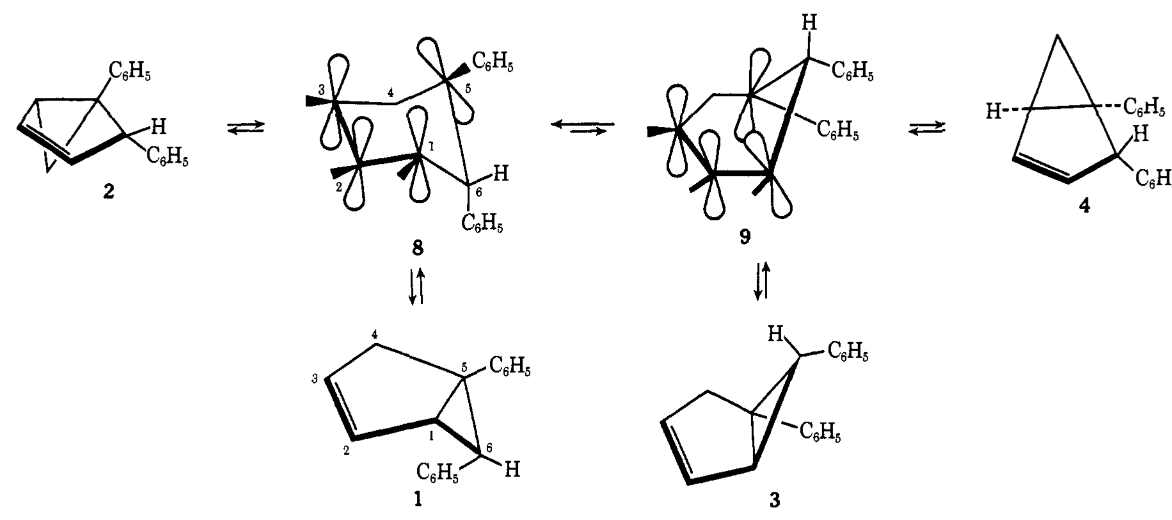
(3) J. S. Swenton, A. L. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970).

(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 122.

(5) Neither of the cis compounds, **3** or **4**, was detected in the kinetic determinations on *trans*-**1**. The estimated error in the rate constants is ±6%.

(6) S. Winstein, W. G. Young, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

(7) If the integrated first-order rate expression over 4% reaction were used in determining the rate constants, apparent good plots of $\ln C_0/C$ *vs.* t result (correlation coefficients = 0.97–0.99). However, in view of the difficulty of detecting curvature in first-order plots at 0–4% reaction, the rate constants from this procedure are considered less reliable than those reported in Table II. The values obtained from the inte-



The stereospecific reaction of *trans*-olefin **1** can be viewed as either a concerted vinylcyclopropane rearrangement or a stepwise process in which ring closure in the diradical is faster than rotation about the $C_{5,6}$ bond.[8] While several groups[1g,i,j] have presented results favoring the intermediacy of a diradical in the vinylcyclopropane–cyclopentene rearrangement, evidence on the mechanism of thermolyses in cyclic systems is less accessible. However, both Eastman and Doering have proposed that rearrangements in the thujene series proceed *via* diradical intermediates.[10] Using the activation energy for the isomerization of *trans*-2-thujene as a model, the calculated minimum activation energy for rearrangement of **1** *via* the diradical path would be 44.0–12.5 (benzylic resonance energy[12]) = 31.5 kcal/mol. In view of the errors involved in the measurement of activation and resonance energies, the experimental value of 32.4 kcal/mol for isomerization of **1** is in agreement with that expected for the two-step process.[13]

The remaining point to be explained is the stereospecific conversion of **1** to **2** in a nonconcerted process. The trivial possibility that this merely reflects the thermodynamic stability of the trans olefins relative to their cis isomers can be readily dismissed from the equilibration results recorded in Table III. Since **3** is the thermodynamic isomer, its absence in the thermolysis of **1** is a result of kinetic control of products. The stereospecific thermolysis of **1** can best be understood by reference to the diradical **8**. In proceeding from **1** to the diradical **8**, molecular models suggest no pronounced changes in steric interactions. Closure of **8** by overlap of the top lobe of the p orbital at C_5 with the allylic center at C_1 ($C_{1,5}$ bonding) regenerates **1**, while closure at C_3 ($C_{3,5}$ bonding) yields **2**. To produce the cis olefins **3** and **4** requires a rotation in diradical **8** to yield **9**. In the course of the **8** → **9** transformation, steric interaction between the two phenyl groups is substantially increased. This is especially acute since the phenyl moiety must remain coplanar with the radical center at C_5 for maximum benzylic stabilization. Thus, the stereospecificity arises from the energy barrier separating the biradicals **8** and **9**.

Table III. Equilibration of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-enes at 201°

Starting isomer	Time, hr	% **1**	% **2**	% **3**	% **4**
1	16.5	34	22	38	6
1	24	33	22	38	7
3	19	33	21	37	8
3	43	34	22	37	7

The thermolysis of **3** is also conveniently viewed in diradical framework. In **3** the phenyl groups are essentially gauche to each other. As the cyclopropane bond is cleaved, the ring approaches the diradical structure **9** in which the phenyl groups are nearly eclipsed. In the case of the cis isomer, rotation to give **8** is competitive with ring closure at the tempera-

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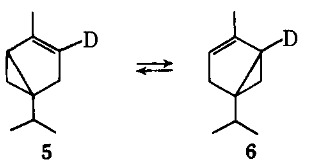
grated first-order equations are: 180.0°, $k_3 = 1.49 \times 10^{-5}$ sec^{-1}; 194.0°, $k_3 = 6.50 \times 10^{-5}$ sec^{-1}; 212.0°, $k_3 = 25.8 \times 10^{-5}$ sec^{-1}. These values yield the general rate expression, $k_3 = 10^{13.4}e^{-37.6/RT}$.

(8) In general, the rate of rotation (k_r) is comparable to the rate of closure (k_c) in acyclic diradicals. However, k_r/k_c varies with structure and k_r/k_c ratios from 0.086 to 12.2 have been noted in thermal reactions.[9]

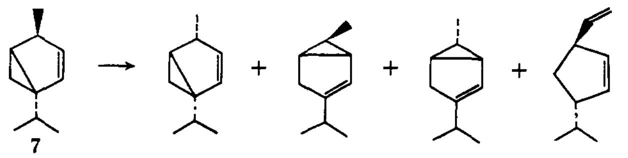
(9) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(10) Thermolysis of α-thujene (**5**) leads to both racemization and deuterium exchange with $k_{rac} = 2k_{rearr}$[11] and $k_{rac} = 10^{12.4}e^{-39,600/RT}$ sec^{-1}.[2c] Eastman[2c] has also shown that *trans*-2-thujene (**7**) undergoes



5 **6**

thermal rearrangement to give the same ratio of products as that derived from *cis*-2-thujene. The rate of disappearance of *trans*-2-thujene was expressed as $10^{14.6}e^{-44,000/RT}$.



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(11) For a discussion see J. Gajewski in "Mechanism of Molecular Migration," Vol. 4, Wiley, New York, N. Y., in press.

(12) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 650 (1966).

(13) The use of α-thujene as a model leads to a predicted minimum activation energy of 27.1 kcal/mol. While this shows more disagreement with the observed value for **1**, it strongly supports our contention that **1** rearranges *via* a diradical mechanism. It would appear unreasonable that the activation energy calculated from α-thujene reacting in a diradical manner would be lower than that for **1** reacting in a concerted process.

ture needed for thermolysis. It is necessary to invoke two such diradical species for the cis thermolyses to account for the different kinetic distribution of products when **1** and **3** are thermolyzed at the same temperature (180°). Presumably, the higher activation energy noted for rearrangement of **3** reflects the inability of the C_5 phenyl group to adopt the most favorable conformation for benzylic stabilization in the transition state due to steric interference from the C_6 phenyl group.

The results noted here demonstrate a rate instance of stereospecificity arising from slow rotation relative to ring closure in a biradical system.[14] In addition, this work may also have significance in understanding the nearly exclusive trans diphenyl stereochemistry in triplet photochemical reactions involving phenyl migration and resulting cyclopropane ring formation.[15]

Acknowledgment. We gratefully acknowledge support from the Merck Company, Rahway, N. J.

(14) Two instances of substituted tetramethylene diradicals having large k_{cyc}/k_{rot} values have been reported: P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, 90, 5317 (1968); J. A. Berson, D. C. Tompkins, and G. Jones, *ibid.*, **92**, 5799 (1970).

(15) Reference 3 and papers cited therein.

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Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds.[1] III. Hydridonitrosyltris(tertiary phosphine) Complexes of Ruthenium and Osmium. Synthesis, Stereochemical Nonrigidity, and Catalytic Properties[2]

Sir:

Transition metal nitrosyl complexes have recently found use as soluble catalysts in reactions such as olefin disproportionation[3] and hydrogenation.[4] The mode of the catalysis by these complexes may result from a facile redox process between the metal and the nitrosyl ligand which causes favorable stereochemical or structural changes about the metal.[4,5] We wish to report the synthesis of a series of nitrosyl complexes, $MH(NO)P_3$ (M = Ru, Os; P = tertiary phosphine), and studies of their stereochemical nonrigidity and catalytic properties in solution.

The complexes I–IV (Table I) are prepared in high yield by reducing the corresponding $Ru(NO)Cl_3P_2$ species[6] with refluxing ethanolic KOH in the presence of excess P. The osmium complexes V and VI are similarly prepared using 2-methoxyethanol as solvent. The deep brown crystalline compounds were characterized by elemental analysis and infrared and ^{1}H nmr spectroscopy (Table I).

The solid-state infrared spectra show absorption in the region 1900–2050 and 1600–1655 cm^{-1} assignable to ν_{M-H} and ν_{N-O} modes, respectively. Deuteration of I, III, and IV (*vide infra*) causes disappearance of the ν_{M-H} mode and a shift of the ν_{N-O} to higher frequency, the magnitude and direction of which implying a resonance interaction between the $\nu_{M-H(D)}$ and ν_{N-O}. This strongly indicates a trans arrangement of hydride and nitrosyl ligands[7] and the idealized (C_{3v}) structure A is proposed for I, III, and IV *in the solid state*[8] (Figure 1).

The ^{1}H nmr spectra of I and VI in CH_2Cl_2 both show a quartet to high field for the hydride resonance which is unchanged from −100 to +80°. Structure A is thus retained for I and VI in solution with $^{2}J_{P-H}$ also being consistent with hydride cis to the phosphine ligands.

The ^{1}H nmr of II in CH_2Cl_2 at 30° shows a narrow singlet for the hydride resonance and, on addition of free PPh_2Me, no detectable change in the spectrum occurs except for the appearance of the free phosphine resonance. Rapid *intermolecular* phosphine exchange is thus not occurring. The hydride resonance remains a singlet on cooling, but below −90° broadens, and at *ca.* −110° a poorly resolved 1:2:2:2:1 spectrum emerges centered at τ 15.0.[9] This low-temperature spectrum is consistent with a structure having two phosphines cis to the hydride ($^{2}J_{P-H} = \pm 32$ Hz) and the remaining phosphine trans or transoid to the hydride ($^{2}J_{P'-H} = \mp 64$ Hz). Intramolecular equilibration of the phosphine ligands[1] above −90° averages the observed $^{2}J_{P-H}$ to zero (since $^{2}J_{P-H} = -{}^{1}/_{2}\,{}^{2}J_{P'-H}$) giving an apparent singlet. Similar observations[10] are found for the analogous osmium complex VI.

Of the possible idealized (C_s) structures for II (and VI) in solution, B, C, and D are considered the most favorable.[11]

The ^{1}H nmr spectrum of III in CH_2Cl_2 at 30° shows a quartet for the hydride resonance (see Figure 2). The spectrum is both solvent and temperature dependent. As the temperature is lowered, the quartet narrows (*i.e.*, the observed $^{2}J_{P-H}$ diminishes) but does not collapse, and concomitantly the resonance shifts downfield. Below −48° however, broadening and collapse of the resonance occur.[12] These (and other[13]) observations indicate that, between +29 and −48°, two isomers[14] are populated in solution, which rapidly interconvert *via* an intramolecular process. This pro-

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(1) Part I, J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, **92**, 6976 (1970); part II, D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, in press.

(2) Work supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

(3) (a) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, **92**, 528 (1970); (b) W. B. Hughes, *ibid.*, **92**, 532 (1970).

(4) J. P. Collman, N. W. Hoffman, and D. E. Morris, *ibid.*, **91**, 5659 (1969).

(5) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., p 573.

(6) (a) M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966); (b) J. Chatt and B. L. Shaw, *ibid.*, *A*, 1811 (1966).

(7) *Cf.* L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966).

(8) Similar, though not identical, shifts are also found in solution (CH_2Cl_2), indicating that A is appreciably populated in solution also.

(9) Since the resonance remains centered about τ 15.0 throughout, clearly no significant population of any other isomer in solution occurs.

(10) In VI, $|2\,{}^{2}J_{P-H} + {}^{2}J_{P'-H}|/3 = 7$ Hz, and a narrow quartet is observed down to −50° at which broadening of the resonance occurs. We have not been able to obtain a satisfactory limiting spectrum, as yet.

(11) In absence of steric constraints the nitrosyl ligand would be expected to occupy an equatorial site in TBP or apical site in SP idealized geometries. B, C, and D are also consistent with the observed coupling constant data.

(12) The limiting spectrum has not yet been obtained because of solubility difficulties.

(13) Infrared studies in CH_2Cl_2 (+30 to −25°) show that on cooling, the band at 1990 cm^{-1} increases at the expense of the 1975-cm^{-1} absorption. Although separate ν_{N-O} modes have not been resolved, the envelope shifts to lower frequency on decreasing the temperature. Under identical conditions, the spectrum of I remains unchanged.

(14) Although the presence of more than two isomers in solution cannot be excluded, the nmr and ir data presently at hand can be adequately interpreted in terms of *only* two isomers, and further isomers need not be postulated at this point.