B. Sims of the Department of Chemistry, University of Arkansas, Dr. Richard M. Jones of this laboratory, and Professor Rolf Huisgen, of the University of Munich.

References and Notes

(1) Research sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with the Union Carbide Corp.

(2) (a) R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391–3404 (1969); (b) R. Huisgen, L. A. Feiler, and P. Otto, *ibid.*, **102**, 3405–3427 (1969); (c) L. A. Feiler and R. Huisgen, *ibid.*, **102**, 3428–3443 (1969); (d) R. Huisgen, L. A. Feiler, and P. Otto, *ibid.*, **102** 3444–3459 (1969); (e) R. Huisgen, L. A. Feiler, and G. Binsch, *ibid.*, **102**, 3460–3474 (1969); (f) R. Huisgen and P. Otto, *ibid.*, **102**, 3475–3485 (1969); (g) R. Huisgen and H. Mayr, *Tetrahedron Lett.*, 2965, 2969 (1975); (h) M. Rey, S. Roberts, A. Dietternbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417–432 (1970); (i) U. A. Huber and A. S. Dreiding, *ibid.*, **53**, 495–513 (1970); (j) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589–590 (1970); (k) P. R. Brook and J. G. Griffiths, *ibid.*, 1344 (1970); (l) W. T. Brady, F. H. Parry III, R. Roe, Jr., and E. H. Hoff, Jr., *Tetrahedron Lett.*, 819 (1970); (m) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mallet, *Tetrahedron*, **27**, 615–633 (1971); (n) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970, pp 164–168.

(3) J. E. Baldwin and J. A. Kapecki, *J. Am. Chem. Soc.*, **92**, 4874 (1970).

(4) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958). (b) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964); *J. Chem. Phys.*, **45**, 2618 (1966).

(5) E. K. von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969), reported that, during the addition of $CH_2{=}CDOC_2H_5$ and $CHD{=}CHOC_2H_5$ to dimethyl azodicarboxylate, the k_H/k_D's were 1.12 and 0.80, respectively, results similar to those of Baldwin and Kapecki.[3]

(6) (a) V. F. Raaen, A. K. Tsiomis, and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 5502 (1960). (b) V. F. Raaen, T. K. Dunham, D. D. Thompson, and C. J. Collins, *ibid.*, **85**, 3497–3499 (1963). (c) C. J. Collins and M. H. Lietzke, *ibid.*, **81**, 5379 (1959); V. F. Raaen and C. J. Collins, *Pure Appl. Chem.*, **8**, 347–355 (1964). (d) C. J. Collins, *Ann. N.Y. Acad. Sci.*, **84**, 603–607 (1960). (e) B. M. Banjamin and C. J. Collins, *J. Am. Chem. Soc.*, **95**, 6145 (1973); (f) V. F. Raaen, T. Juhlke, F. J. Brown, and C. J. Collins, *ibid.*, **96**, 5928–5930 (1974); (g) C. J. Collins, B. M. Benjamin, M. Hanack, and H. Stutz, *ibid.*, **99**, 1669 (1977).

(7) Styrene-α-^{14}C and styrene-β-^{14}C were prepared from aceto-*1*-^{14}C-phenone and aceto-*2*-^{14}C-phenone, respectively (G. A. Ropp, V. F. Raaen, and A. J. Weinberger, *J. Am. Chem. Soc.*, **75**, 3694 (1953)) followed by reduction with lithium aluminum hydride to yield the appropriate methyl phenylcarbinols. The latter were dehydrated in the presence of fused potassium bisulfate to yield $Ph{}^*CH{=}CH_2$ and $PhCH{=}{}^*CH_2$ (L. A. Brooks, *ibid.*, **66**, 1295 (1944); see also A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part I, Interscience, New York, N.Y., 1958, pp 836–838). *cis*-β-Deuteriostyrene was prepared from phenylacetylene-*d* (obtained on treatment of $PhC{\equiv}CLi$ with D_2O) by treatment with diisobutylaluminum hydride (Alfa Division of Ventron Corp.) by a modification of the procedure of G. Zweifel, *J. Am. Chem. Soc.*, **92**, 668 (1970). *trans*-β-Deuteriostyrene was prepared from phenylacetylene and diisobutylaluminum hydride followed by decomposition of the β-phenylethyldiisobutylaluminum with D_2O.

(8) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

(9) A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964).

(10) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Cook, *J. Am. Chem. Soc.*, **94**, 1364 (1972).

(11) A. J. Kresge, N. N. Lichtin, and K. N. Rao, *J. Am. Chem. Soc.*, **85**, 1210 (1963); A. J. Kresge, N. N. Lichtin, K. N. Rao, and R. E. Weston, Jr., *ibid.*, **87**, 437 (1965).

Clair J. Collins*

Oak Ridge National Laboratory, Oak Ridge, Tennessee and the Department of Chemistry, University of Tennessee Knoxville, Tennessee 37916

Ben M. Benjamin

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

George W. Kabalka

Department of Chemistry, University of Tennessee Knoxville, Tennessee 37916

Received November 11, 1977

Effects of Liquid Crystal Solvents on the Photodimerization of Acenaphthylene

Sir:

The effects of media on thermal and photochemical reactions have received much attention in recent years. The utility of monolayers,[1] micelles,[2] and, in particular, liquid crystals[3] to probe environmental influences on chemical reactivity has been demonstrated.

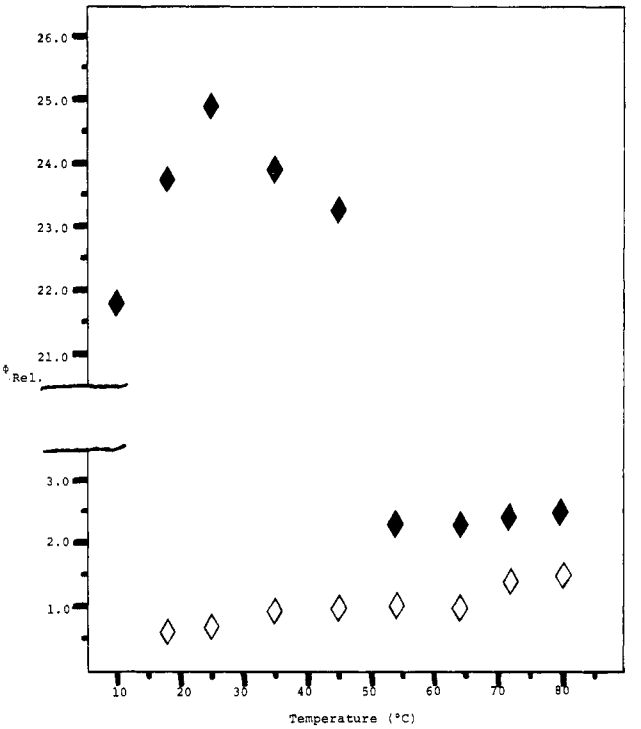
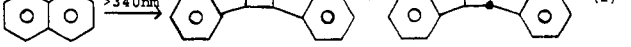


Figure 1. Φ_{Rel} vs. temperature for dimerization of 0.08 M acenaphthylene in *n*-butyl stearate (◇) and the cholestanyl ester mixture (◆). Φ_{Rel} is defined as $\Phi_{solvent}/\Phi_{toluene}$ at each temperature. Each point is the average of at least duplicate measurements.

Here, we report what we believe to be (1) the largest rate enhancement of any bimolecular reaction conducted in a liquid crystal, and (2) the first example of a pitch controlled reaction rate in a cholesteric phase.[4]

The photodimerization of acenaphthylene is known[5] to yield its *syn*- and *anti*-cyclobutane dimers (eq I). The product distribution has been suggested to be state and solvent dependent.[6]



Quantum yields and product distributions[7] have been determined here in toluene, *n*-butyl stearate, and a 1:1 mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate[8] as a function of temperature, solvent phase, and concentration of starting material. Nitrogen saturated samples in sealed Pyrex capillary tubes were thermostated and irradiated (λ >340 nm) to 10–15% conversion in a miniature merry-go-round apparatus. Analyses of percent conversions (and, in some cases, product distributions) were performed conveniently by UV spectroscopy.[9]

The relative quantum yields for the dimerization of 0.08 M acenaphthylene in the three solvents as a function of temperature are shown in Figure 1. Absolute quantum yields[10] for dimerization (~10% conversion) of 0.08 M acenaphthylene at 366 nm in toluene are 0.011, 0.012, and 0.012 at 25, 35, and 55 °C, respectively. The quantum yield obtained at 25 °C is near the value (0.0135) reported by Livingston and Wei[5b] for reaction under conditions similar to ours.

As can be seen, the quantum efficiency in *n*-butyl stearate (Φ_s), which exhibits a smectic phase below 25 °C,[11] varies slightly as a function of temperature and remains near the efficiency observed in toluene solutions (Φ_t). This similarity is unexpected if solvent viscosity alone determines the dimer-

0002-7863/78/1500-2571$01.00/0 © 1978 American Chemical Society

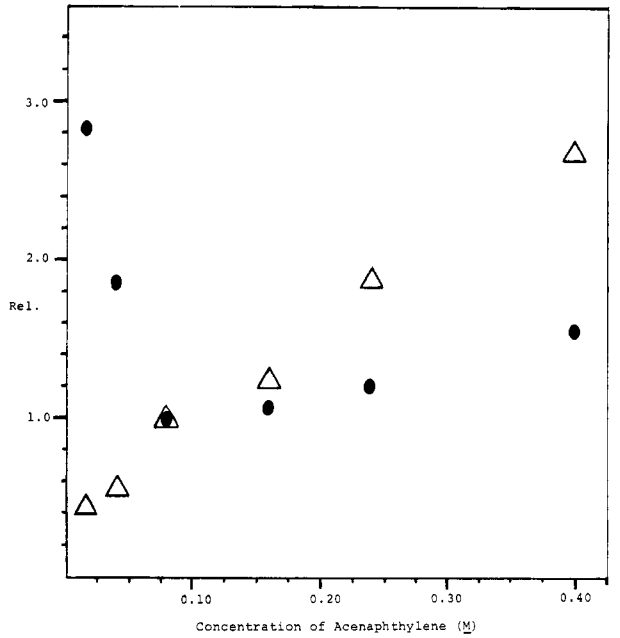


Figure 2. Φ'_{Rel} vs. concentration of acenaphthylene at 35 °C (●) and 55 °C (△). Φ'_{Rel} is defined as the ratio of the dimerization quantum efficiency at a given initial concentration of acenaphthylene divided by the quantum efficiency for an initial concentration of 0.08 M acenaphthylene at a given temperature. Each point is the average of at least duplicate measurements.

ization rates at a given temperature and suggests that solvent order is enhancing the fraction of encounters that result in dimerization.

The effect of solvent phase on the quantum yield for dimerization in the cholestanyl ester mixture (Φ_c) is more dramatic. In the isotropic phase from 55 to 80 °C, Φ_c/Φ_t remains ~2.5. However, in the cholesteric phase from 10 to 45 °C, Φ_c/Φ_t is 21–25 at 0.08 M acenaphthylene. When 0.016 M acenaphthylene is employed at 35 °C, *the quantum yield in the cholesteric liquid crystal is* 74 Φ_t.

Although no firm evidence for their existence has been found, ground-state complexes have been suggested to be involved in the dimerization mechanism for acenaphthylene.[5b,6c,12] If such a complex were important in the cholesteric solvent, the rate data at 0.08 M acenaphthylene would require that association be much more favored in the cholesteric phase than in the isotropic phase. The formation of aggregates should have three major effects on the dimerization: (1) at a given concentration, the dimerization should proceed more rapidly than in toluene; (2) as the acenaphthylene concentration is increased, the rate of dimerization should increase more rapidly than is estimated from diffusion based arguments; (3) the percentage of the syn product, at a given concentration of acenaphthylene and percent conversion, should be greater in the cholesteric solvent than in toluene.

The increase in the relative quantum yield with decreasing temperature (Figure 1) reveals that the first effect is realized. However, the data of Figure 2 indicate that the second effect is not. At 55 °C, Φ_c increases linearly as a function of initial acenaphthylene concentration. In the cholesteric phase at 35 °C, Φ_c *decreases* as the concentration of acenaphthylene is increased from 0.016 M to 0.08 M and *increases* as the concentration is increased from 0.08 M to 0.40 M. The decrease in Φ_c with increasing concentration of acenaphthylene is incompatible with a model in which ground-state aggregation is significant.

Product distributions were determined for dimerization of 0.08 M acenaphthylene at 35 °C in the three solvents. In toluene solutions, the syn isomer represents ~95 and 60% of total dimer at 35 and 65% conversion, respectively. The syn remains ~60% of the dimer over 25–55% conversion in *n*-butyl stearate solutions. Similarly, in the cholesteric liquid crystal solvent, the syn isomer varies slightly (~60% to 40%) as the percent conversion increased from 25 to 75%.

Singlet dimerization of acenaphthylene in isotropic solvents is known to yield almost exclusively the syn dimer, while the triplet reaction results in a mixture of the syn and anti isomers.[5,6] Therefore, in toluene solutions, the singlet reaction (whether from dynamic encounters or ground-state complexes) maximizes at lowest percent conversions of acenaphthylene. The triplet reaction increases in importance as the dimerization proceeds and is responsible for the decrease in the syn/anti ratio. The cholesteric liquid crystal and *n*-butyl stearate, being highly viscous, will discourage bimolecular encounters prior to intersystem crossing of the singlets. Although the highly ordered cholesteric solvent may alter the syn/anti ratio obtained from the singlet and triplet dimerizations, the *n*-butyl stearate, which is not highly ordered at 35 °C, should not. The similarity between the product ratios in *n*-butyl stearate and the cholesteric solvent strongly suggests enhanced triplet reaction, not solvent-order or ground-state complexes, as being responsible for the relatively low syn/anti ratios.

The cholesteric–isotropic transition temperatures and melting points of the cholestanyl esters doped with acenaphthylene vary inversely with solute concentration as expected,[13] and ORD spectra of thin films (0.025 mm) of these mixtures show systematic concentration dependent variations. The positive dispersion of the pure solvent decreases to zero and becomes negative as the solute concentration increases. The nematic point[14] is observed at an acenaphthylene concentration close to the Φ_c minimum at 35 °C in Figure 2.

The solute concentration exerts two influences on Φ_c in the cholesteric phase. The first is a kinetic effect: according to a simple kinetic scheme for a photodimerization, the rate of product formation should increase linearly with concentration at constant light intensity. The second is an ordering effect: the "layered" structure of the cholesteric phase, which influences the orientation of solute–solute collisions, is altered by variations in solute concentrations.

Φ_c should depend upon the number of ground-state molecules encountered by each excited-state acenaphthylene during its lifetime, as well as the orientation of such collisions. The increase in solvent pitch as the concentration is increased from 0.016 M to 0.08 M should decrease the probability of two solute molecules colliding with the preferred, plane parallel, geometry. The total number of collisions per unit time should, however, increase as the concentration is increased. The low concentration portion of Figure 2 at 35 °C, therefore, reveals that the order effect dominates Φ_c in this region and that the fraction of collisions leading to dimer decreases rapidly as the concentration is increased. At acenaphthylene concentrations >0.08 M where Φ_c increases, the fraction of collisions leading to dimerization is greater than in the isotropic phase but the number of collisions per unit time is lower owing to the greater viscosity of the solvent. The net effect is that Φ_c increases less rapidly with concentration than in the isotropic phase. However, the observation that the absolute magnitude of Φ_c is greater in the cholesteric phase than in the isotropic phase indicates that the order effect is more important than the kinetic effect. From these results and the product distribution studies we conclude that solvent order exerts a dramatic influence on the efficiency of dimerization, i.e., the fraction of collisions leading to product, but plays little or no role in determining the stereochemical course of the reaction.

The dramatic effects of solvent phase described here demonstrate the tremendous potential of liquid crystals in elucidating reaction mechanisms and governing reaction rates. With a more detailed knowledge of the effects of size, shape, and

concentration of solute molecules on the pitch of the cholesteric solvent, it should be possible to increase the rates and specificities of some reactions, decrease the rates, and redirect the stereochemical courses of others. We shall report such examples in future publications.

Acknowledgment. We thank Drs. Wolfgang Elser and Daniel Martire for helpful discussions concerning this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to The National Science Foundation (Grant No. CHE76-84120), and to the Naval Research Laboratory (Grant No. N00173-77-C-0077) for support of this research.

References and Notes

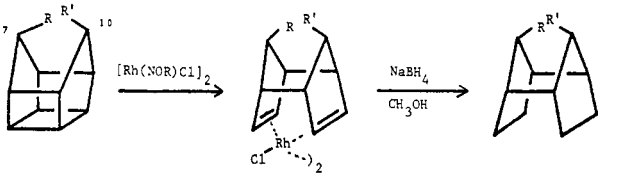
(1) (a) F. H. Quina, D. Möbius, F. A. Carroll, F. R. Hopf and D. G. Whitten, *Z. Physik. Chem. Neue Folge*, **101**, 151 (1976); (b) F. H. Quina and D. G. Whitten, *J. Am. Chem. Soc.*, **99**, 877 (1977).
(2) W. H. Waddell, A. P. Yudd, and K. Nakinishi, *J. Am. Chem. Soc.*, **98**, 238 (1976).
(3) (a) W. H. Pirkle and P. L. Rinaldi, *J. Am. Chem. Soc.*, **99**, 3510 (1977); (b) W. E. Bacon, *J. Phys., Suppl. 3*, C1-409 (1975); (c) L. Verbit, T. R. Halbert, and R. B. Patterson, *J. Org. Chem.*, **40**, 1649 (1975); (d) F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Am. Chem. Soc.*, **97**, 204 (1975); (e) M. J. S. Dewar and B. D. Nanlovsky, *ibid.*, **96**, 460 (1974).
(4) Such effects have been sought previously and not been found.[3a]
(5) (a) I. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967); (b) R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967).
(6) (a) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); (b) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **89**, 3068 (1967); (c) D. O. Cowan and R. L. Drisko, *ibid.*, **92**, 6286 (1970); (d) D. O. Cowan and R. L. Drisko, *ibid.*, **92**, 6281 (1970); (e) D. O. Cowan and J. C. Koziar, *ibid.*, **96**, 1229 (1974); (f) D. O. Cowan and J. C. Koziar, *ibid.*, **97**, 249 (1974).
(7) Syn/anti product ratios were not calculated in experiments carried to 10–15% conversions of acenaphthylene: overlap of the ultraviolet spectra of the monomer with both dimers precludes an accurate determination of either dimer independently. Small changes in the total optical density at a given wavelength result in large variations in the calculated product ratio. Under our irradiation conditions, the dimers neither interconvert nor reconvert to acenaphthylene.
(8) The cholestanyl mixture, mp 71–72 °C, exhibits a monotropic liquid crystalline phase from 54 to <10 °C. It was utilized here owing to its thermal and photochemical stability. The complete phase diagram will be reported in a full paper.
(9) The details of the experimental procedure and spectral data on starting materials and products will be reported in a full paper.
(10) Nitrogen-saturated toluene solutions of acenaphthylene were irradiated in duplicate in a merry-go-round apparatus with a 450-W medium-pressure mercury arc using Corning No. CS-054 and CS-737 filters. Ferrioxalate solutions at 25 °C were employed as the actinometers.
(11) D. Krishnamurti, K. S. Krishnamurthy, and R. Shashidar, *Mol. Cryst. Liq. Cryst.*, **8**, 339 (1969).
(12) (a) V. A. Crawford and C. A. Coulson, *J. Chem. Soc.*, 1990 (1948); (b) E. J. Bowen and J. D. F. Marsh, *ibid.*, 109 (1947).
(13) T. Novak, E. J. Poziomek, and R. A. Mackay, *Mol. Cryst. Liq. Cryst.*, **20**, 203 (1973).
(14) I. Tencher, K. Ko, and M. M. Labes, *J. Chem. Phys.*, **56**, 3308 (1972).

Jeanne M. Nerbonne, Richard G. Weiss*
Department of Chemistry, Georgetown University
Washington, D.C. 20057
Received December 19, 1977

Long-Range Steric Effects in Rhodium(I) Cleavages of Secopentaprismanes. A Reversible Rhodium(I)-Mediated Cyclobutane–Diolefin Conversion[1]

Sir:

We have found that rhodium(I) complexes of *syn*-tricyclo[4.2.1.$1^{2,5}$]deca-3,7-dienes can be prepared readily by rhodium(I)-induced cleavage[2] of the strained secopentaprismane cage system.[3] Thus, secopentaprismane (**1**, mp 108–109 °C) reacts with an equivalent of $[Rh(NOR)Cl]_2$ in chloroform at 70 °C to give **2** and free norbornadiene. The structure of the ligand in **2**, as drawn, is fully consistent with the NMR spectra of the complex: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.26 (4 H, br s), 2.65 (4 H, br s), 1.65 (2 H, d, J = 12 Hz), 1.34 ppm (2 H, d, J =12 Hz); ^{13}C NMR (22.63 MHz, proton decoupled, Me_2SO-d_6) δ 88.0 (4 C, J_{Rh-C} = 15 Hz), 45.0 (4 C), 43.3 ppm (2 C, J_{Rh-C} = 3 Hz). Similarly, the reaction of 7-*endo*-methylsecopentaprismane (**3**) with $[Rh(NOR)Cl]_2$ was shown to give the diene complex **4**.[4]



1, R=R'=H
3, R=H; R'=CH_3
[**6**, R=R'=CH_3]
7, R=R'=OAc

2, R=R'=H
4, R=H; R'=CH_3
8, R=R'=OAc

5, R=R'=H
9, R=R'=OAc

Complexes **2** and **4** are quite stable. The diene ligand is not displaced by CO, phosphines, or norbornadiene at a useful rate. As the metal is ligated tightly, the cleavage reaction is not catalytic in rhodium(I), unlike the related reactions of cubane[2a] and homopentaprismane.[2c] The complexes are reduced readily by sodium borohydride in methanol;[5] for example, reduction of **2** gives rhodium metal and *syn*-tricyclo[4.2.1.$1^{2,5}$]decane (**5**) in nearly quantitative yield: ^{1}H NMR δ 2.28 (4 H, br s), 1.77, 1.69 (6 H, centers of overlapping multiplets), 1.18 (4 H, br d), 0.45 ppm (2 H, br d); ^{13}C NMR ($CDCl_3$) δ 36.0, 29.6, 25.7 ppm.[6] The cleavage and reduction reactions are quite general and offer special synthetic opportunities; access to the *syn*-tricyclo[4.2.1.$1^{2,5}$]decane system is otherwise very limited.[7] In this communication, however, our concern is with the extraordinary effects of methano bridge substituents on the reactivity of the secopentaprismanes and the related complexes.

The rates of cleavage of **1** and **3** by an equivalent of Rh(NOR)acac[8] in $CDCl_3$ at 50 °C were measured by standard ^{1}H NMR techniques. Both reactions appear cleanly second order to at least 90% completion: for **1**, $k_2 = 1.3 \times 10^{-2}$ L mol^{-1} s^{-1}; for **3**, $k_2 = 1.3 \times 10^{-3}$ L mol^{-1} s^{-1}. The tenfold decrease in second-order rate constant resulting from the introduction of a methyl group well away from the reaction site is remarkable. Even more so is the fact that introduction of a second *endo*-methyl group stops the reaction altogether; we cannot detect reaction of 7-*endo*,10-*endo*-dimethylsecopentaprismane (**6**, mp 88–89 °C) with Rh(NOR)acac even under conditions more severe than those used for the cleavage of **1** and **3**.

We suggest that the effect of *endo*-methyl groups so far from the site of ring cleavage arises in steric interference to the intranuclear movements which accompany opening of the cage. The bridgehead atoms, C-1, C-6, C-8, and C-9, act as pivots transmitting movement within these fairly rigid molecules. The moving apart of C-2, C-5 and C-3, C-4 that must occur as the cage cyclobutane rings are broken results, via these pivots, in the methano bridges (and their endo substituents) moving toward one another. This becomes energetically more difficult as the endo substituents increase in number and/or effective size. Apparently, steric compression would become so severe in the *endo*-dimethyl case that even the great exothermicity of the cage cleavage is insufficient to drive the reaction significantly forward.[9]

Such long-range steric effects probably also account for the lack of reactivity of diene complexes like **2** and **4** in ligand exchange reactions. We suspect that, if the diene were to come free of the metal, steric compression at the methano bridges would increase. Again the point being that energetically favorable increases in distance (d) between C-2, C-5 and C-3, C-4 engender, by way of the bridgehead pivot atoms, unfavorable decreases (d′) between the atoms on the methano bridges.[10]

0002-7863/78/1500-2573$01.00/0 © 1978 American Chemical Society