Two Factors in Thermal Cis-Trans Rearrangement of Pentaenes: Configuration in (*E*,*E*)-Octahydro-2,2'-bi-3*H*-naphthylidene. Extensivity in 2,2'- and 3,3'-Bicholestadienylidenes

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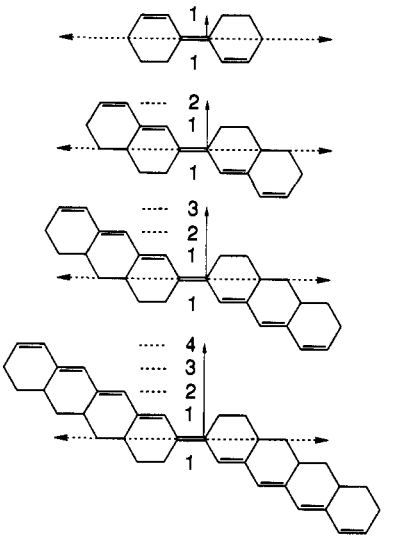
Abstract: Useful interaction between theory and practice in the syn-anti thermal rearrangement of polyenes depends on transferability of theoretically calculated enthalpies of activation, which are intrinsically gas-phase, to experiment, which are most often conducted in solution. The choice of all-trans polyenes for further experimental extension of our limited knowledge led us to worry how coupling of motions required to attain the transition state with motions and translocations in the solvent might cause the resulting activation parameters to deviate from their hypothetical gas-phase values. We have compared two isomeric pentaenes that present substantial differences in the degree of their extension into the solvent; that is, in their "extensivity". Because our pragmatically selected substrates 2,2'- and 3,3'-bicholestadienylidenes (**2** and **3**, respectively) did not have identical configurations, model compounds (*E*,*Z*)-**5** and (*E*,*E*)-**5** were compared and found to have $\Delta H^{\ddagger}$ = 34.0 and 32.1 kcal/mol, respectively. An even greater difference between **2** and **3**, 36.1 and 31.6 kcal/mol, respectively, points to an additional factor. We have apportioned the discrepancy between a configurational factor of 1.9 kcal/mol and an "extensivity" factor of 2.6 kcal/mol. This latter factor is tentatively ascribed to the operation of Kramers' dynamical concept of solvent friction.

In the preceding paper,[1] initial steps were taken to see what happens to the rate of thermal cis-trans isomerization about a double bond as the number of conjugated double bonds is increased. Activation parameters for the first three members of the series of semirigid polyenes shown in Scheme I were determined, the fourth to follow.[2] Although the triene that begins the series is sufficiently volatile to be examined in the gas-phase without disturbances of unkown magnitude by the solvent, the following members of the series are not. Given Kramers' pioneering recognition of "solvent friction" as a potential influence on the kinetics of reactions in solution[3] and the theoretical and experimental developments of the last two decades,[4-8] the possibility of a systematically increasing perturbation by solvent in our series became a pressing concern.

Many investigations on the influence of dynamic solvent effects on internal rotational processes reactions of low activation energies, particularly those of Fleming[6] and Barbara[7] and their co-workers, serve brilliantly as warnings to the present investigation. From their study of the cis-trans rearrangement of photoexcited 1,4-diphenylbutadiene, Velsko and Fleming,[6b] for example, conclude "...that part of the activation energy observed in the linear alkanes may be due to solvent hindrance of the large amplitude motion associated with isomerization." By contrast, Tabak and Morawetz,[8] addressing the same question by a comparison of the rates of *cis*-trans isomerization of a monomeric azobenzene and one incorporated in a polyamide, found "no significant difference between the behavior of these residues in the chain molecules and that of their analogs."

Scheme I



Whether solvent friction is influencing the thermal rearrangements of the polyenes in this study is the object of this paper. The first member of the series, a cylindrical triene, rearranges at high temperature and consequently at low density and viscosity of solvent. But succeeding members, which systematically extend their molecular dimensions in the direction perpendicular to their axes of rotation during syn-anti isomerization, rearrange at ever lower temperatures and correspondingly higher viscosities of solvent. This increase in "extensivity" may possibly lead, during the 90° rotation needed to reach the geometry of the transition state, to an ever larger encumbrance by ever larger volumes of solvent and a concomitant systematic increase in the resulting activation parameters over their gas-phase counterparts. Although solvent friction would not detract from the nonaene as a model for the thermal rearrangement *in solution* of the anticarcinogen β-carotene (**1**), it would compromise the series as a quantitative test of theoretical calculations of stabilization energies of polyenic radicals, unless, of course, reliable corrections could be made.

To assess the credibility of the concept, two pentaenes, shown in Scheme II, have been selected. Their precursor ketones are accessible from readily available, optically pure cholesta-4-en-3-one and should be convertible to mixtures of syn and anti products

(1) Doering, W. von E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, in press.
(2) Doering, W. von E.; Sarma, K. Manuscript in preparation.
(3) Kramers, H. A. *Physica (The Hague)*, **1940**, *7*, 284-304.
(4) (a) Hynes, J. T. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC: Boca Raton, FL, 1985; Vol. 4, pp 171-234. (b) Hynes, J. T. *J. Stat. Phys.* **1986**, *42*, 149-168. (c) Northrup, S. H.; Hynes, J. T. *J. Chem. Phys.* **1978**, *69*, 5246-5260; 5261-5266. (d) Ladanyi, B. M.; Hynes, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 585-593.
(5) Truhlar, D. G.; Hase, W. L.; Hynes, J. T. *J. Phys. Chem.* **1983**, *87*, 2664-2682.
(6) (a) Courtney, S. H.; Fleming, G. R. *J. Chem. Phys.* **1985**, *83*, 215-222 and reference cited therein. (b) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553-3562.
(7) Barbara, P. F.; Jarzeba, W. *Acc. Chem. Res.* **1988**, *21*, 195-199 and references cited therein.
(8) (a) Morawetz, H. *Macromolecules in Solution*, 2nd ed.; Wiley: New York, 1975; pp 439-442. (b) Tabak, D.; Morawetz, H. *Macromolecules* **1970**, *3*, 403-410.

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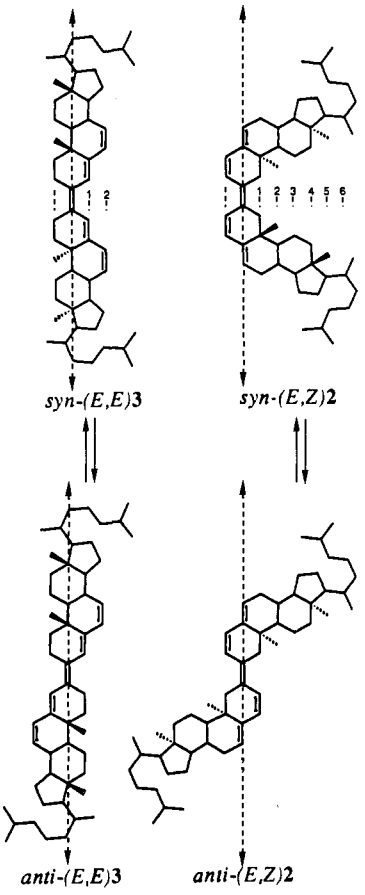
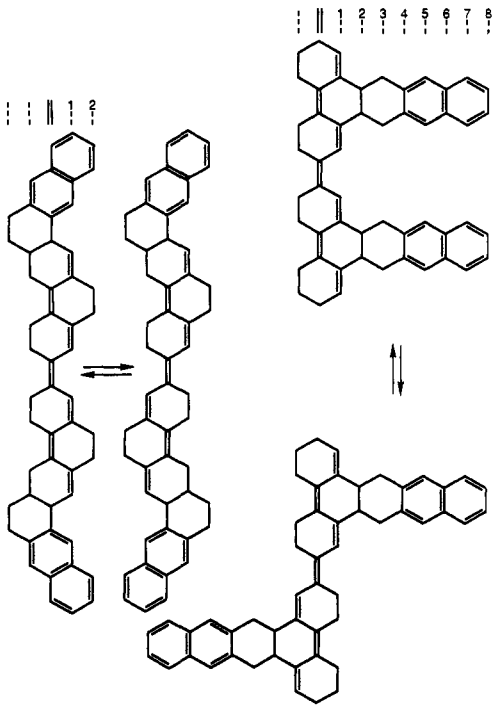
Scheme II



Scheme III



by the Mukaiyama-Tyrlik-McMurry synthesis.[1,9] Clearly far from ideal with their floppy isooctyl tails, 2,2′-bicholesta-3,5-dienylidene (**2**) of high extensivity and 3,3′-bicholesta-4,6-dienylidene (**3**), more or less cylindrical and of low extensivity,

(9) (a) Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041–1044. (b) Tyrlik, S.; Wolochowicz, I. *Bull. Soc. Chim. Fr.* **1973**, 2147–2148. (c) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709. (d) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524.

Scheme IV

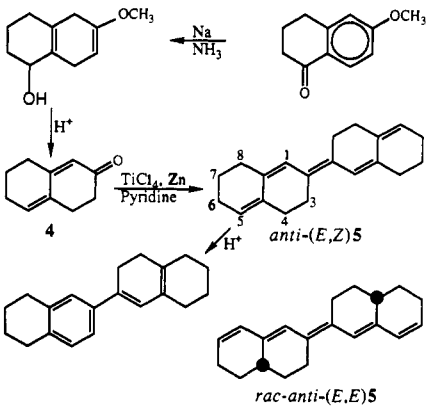


Table I. Ultraviolet-Visible Spectra of Three Conformationally Distinct Pentaenes in Spectrograde Hexanes

compound	λ_{max} (ϵ)[a]		
β-anti-(E,E)-**5**	337 (48 500)	354 (82 100)	374 (81 600)
anti-(E,Z)-**5**	333[b] (44 000)	348 (56 500)	366 (46 000)
syn-(E,Z)-**5**	326[b] (41 000)	340 (53 700)	356 (41 800)

[a] Wavelength in nanometers. [b] Shoulder.

promised to be far easier to come by than a more elegantly designed pair like that in Scheme III. To their further and more serious detraction, **2** and **3** possess pentaene systems of differing configuration: **3** having the all-trans *E,E* and **2** having the *E,Z* configuration, twice over. Sustmann and Schmidt[10] and Walton et al.[11] have found the (*E,E*)-pentadienyl radical to be thermodynamically more stable than its *E,Z* congener. The calculated difference between the two configurations of ~2 kcal/mol compares with an experimental difference[11c] of 2.4 kcal/mol. When combined with a heat of hydrogenation of (*E,E*)-hexa-1,3,5-triene known to be greater than that of the *E,Z* isomer by 1.1 kcal/mol,[12] the enthalpy of activation of isomerization of **2** might be expected to be 2.6 kcal/mol [2(2.4–1.1)] higher than that of **3**.

As prelude to the investigation of the cholestadienylidenes, the influence of configuration has been examined by comparing the pentaenes *syn-* and *anti-(E,Z)*-**5** with *meso-* and *rac-*, *syn-* and *anti-(E,E)*-**5**.[1] This comparison is itself flawed by different degrees of substitution: octa in (*E,Z*)-**5** and hexa in (*E,E*)-**5**, whereas **2** and **3** are both hexasubstituted (Schemes II and IV).

Synthesis of *syn-* and *anti-(E,Z)*-**5** is accomplished by application of the Mukaiyama-Tyrlik-McMurry reaction,[9] as modified by Lenoir,[13] to the dienone **4**, itself prepared following the directions of Gaidamovich and Torgov.[14] Both stereoisomers can be isolated by fractional crystallization and are assigned configuration by nuclear Overhauser enhancement (see Experimental Section). The change from *E,E* configuration to *E,Z* leads to a shift in absorption spectrum to shorter wavelength and lower extinction coefficient (Table I).

The sensitivity of *anti-(E,Z)*-**5** to rearrangement by acid is attested by its conversion, when heated for 7.5 h at 60 °C in deuteriochloroform, to a mixture of aromatic compounds. In the NMR, two doublets at 7.18 and 7.01 ppm (J = 8.6 Hz) and a singlet at 7.13 ppm in the ratio 1:1:1 indicate a 1,2,4-trisubstituted benzene ring (see Scheme IV).

Several control experiments exclude various extraneous, nonthermal reactions that might interfere with study of the kinetics. Rates of conversion of *anti-(E,Z)*-**5** to its syn isomer are

(10) Sustmann, R.; Schmidt, H. *Chem. Ber.* **1979**, *122*, 1440–1447.
(11) (a) Griller, D.; Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 758–759. (b) Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633–641. (c) MacInnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1073–1076.
(12) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. von E.; Roth, W. R.; Schröder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605–8610.
(13) Lenoir, D. *Synthesis* **1977**, 553–554.
(14) Gaidamovich, N. N.; Torgov, I. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1961**, 1682–1687.

Table II. Thermal syn-anti Isomerization of *anti*-2-(3′,4′,6′,7′-Tetrahydro-8′*H*-2′-naphthylidene)-3,4,6,7-tetrahydro-8*H*-naphthalene (*anti*-(*E*,*Z*)-**5**) to *syn*-(*E*,*Z*)-**5** in Benzene-d_6: Rate and Equilibrium Constants and Activation Parameters

T (°C)[a]	$k_1(10^{-6}\ s^{-1})$[b]	K
144.6	1.241 ± 0.011[c]	0.589
144.6	1.265 ± 0.005	0.587
154.2	3.417 ± 0.046	0.597
154.2	3.381 ± 0.037	0.593
166.6	10.06 ± 0.07	0.596
166.6	9.84 ± 0.02	0.598
[166.6[d,e]	10.17 ± 0.37	0.583]
[166.6[f]	10.15 ± 0.14	0.594]
[166.6[g]	10.58 ± 0.09	0.600]
[166.6[h]	11.39 ± 0.52	0.626]
179.2	31.19 ± 0.07	0.611
179.2	31.54 ± 0.02	0.614
192.3	96.50 ± 0.23	0.635

Arrhenius Plot ($1/T$ vs log k)

E_a (kcal/mol)	34.87 ± 0.29
A log	12.35 ± 0.14

Eyring Parameters

$\Delta H^{\ddagger}$ (kcal/mol)[i]	33.99 ± 0.29
$\Delta S^{\ddagger}$ (eu)[i]	−4.82 ± 0.65

Thermodynamics ($1/T$ vs log K)

$\Delta\Delta H°$ (kcal/mol)	0.71 ± 0.08
$\Delta\Delta S°$ (eu)	0.49 ± 0.20

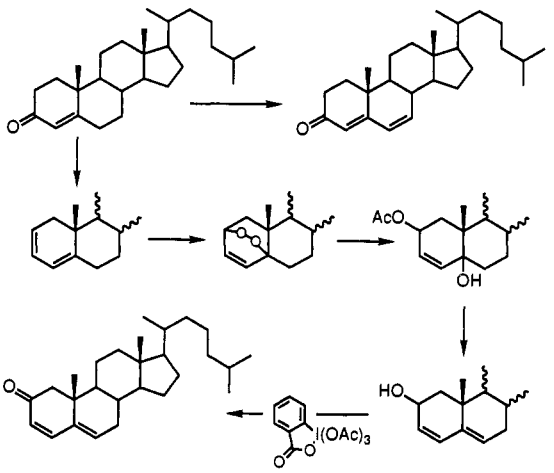
[a] ±0.2 °C. [b] Calculated by linear regression by using the usual expression for reversible first-order reactions: $k_1 + k_{-1} = (1/t)\ln[(x_{eq} - x_0)/(x_{eq} - x)]$; $K = k_{-1}/k_1$. [c] Double all standard errors for 90% confidence limits. [d] Experiments in brackets have not been used in the calculation of activation parameters. [e] In Pyrex instead of Corning 0120. [f] With 9,10-dihydroanthracene (20.1%, w/v). [g] With 1,4-diazobicyclo[2.2.2]octane (0.39%, w/v). [h] With acetic acid (1.0%, v/v); many byproducts. [i] Calculated at 168.5 °C.

the same in lead–potash ampules (Corning 0120), generally used in this study, as in Pyrex ampules. Addition of 9,10-dihydroanthracene, which is an effective trap of free radicals at higher temperatures,[15] has no effect on the rate constant at 167 °C or on recovery (>98.6%). Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) has no effect, a particularly significant control given the sensitivity of the polyenes to acid and a much reduced recovery in acetic acid.

Kinetics are determined as described in the previous paper.[1] Rate and equilibrium constants and activation parameters derived therefrom, recorded in Table II, are based on data relegated to supplementary material (Table V). The slower rate of rearrangement of (*E*,*Z*)-**5** relative to that of (*E*,*E*)-**5**[1] is ascribable entirely to a higher enthalpy of activation: 34.0 kcal/mol compared to 32.1 kcal/mol, respectively.

In addition to having different configurations, (*E*,*Z*)-**5** is octasubstituted, while (*E*,*E*)-**5** is hexasubstituted. This difference may confer a small stabilization on the starting state of (*E*,*Z*)-**5** but would affect the relative rates only if uncompensated in the radical-like transition states. Apposite and reassuring is the deduction from the most recent bond dissociation energies of Seetula, Russell, and Gutman[16] that the imaginary heats of semihydrogenation of the simple olefins ethene, propene, and 2-methylpropene to ethyl, isopropyl, and *tert*-butyl radicals, respectively, are essentially constant: 15.8, 16.5, and 15.6 kcal/mol, respectively. We conclude that degree of substitution is an unlikely contributor to any difference in enthalpies of activation.[17]

Scheme V



The ground-state, cis configurational factor, which makes the heat of formation of *cis*-hexa-1,3,5-triene[12] 1.1 kcal/mol more positive than that of its trans isomer, would be expected to *decrease* the enthalpy of activation of (*E*,*Z*)-**5** by 2.2 kcal/mol. Instead, there is an *increase* of 1.9 kcal/mol. Per pentadienyl radical, (*E*,*E*)-**5** appears to be favored by 2.1 kcal/mol [(2.2 + 1.9)/2], in good agreement with the value 2.4 kcal/mol found by ESR[10,11c] (vide supra). The configurational factor in the thermochemistry of pentadienyl radicals warrants further controlled exploration by the method of cis–trans isomerization.

Both cholestadienones required as educts for the preparation of **2** and **3** are derived from cholest-4-en-3-one. Treatment with chloranil[18] generates cholesta-4,6-dien-3-one in simple fashion. Although isomeric cholesta-3,5-dien-2-one has been prepared by Ruzicka, Plattner, and Furrer,[19] we chose to develop a route, outlined in Scheme V, via cholesta-2,4-diene and its 1,4-peroxide.[22] Reductive coupling by the Mukaiyama-Trylik-McMurry[9] procedure proceeds satisfactorily and leads, thanks to the chiral homogeneity of the starting ketones, to binary mixtures of syn and anti isomers instead of the quaternary mixtures encountered when starting with racemic ketones.[1] To the benefit of the kinetic measurements, it also leads to a non-equilibrium mixture, in which the thermodynamically less stable *syn* configuration is kinetically favored. Felicitous, base line separation of ^{1}H NMR signals of olefinic protons in *syn*- and *anti*-**2** (doublets from C-3 protons at 6.74 and 6.61 ppm) and in *syn*- and *anti*-**3** (singlets from C-4 protons at 6.45 and 6.25 ppm) allows quantitative analysis of mixtures of the four compounds. In principle, mixtures of **2** and **3** can be followed in the same reaction tube under identical conditions. In the event, the difference in their rates of reaction is too large for this technique to offer any significant improvement in accuracy.

Kinetic data from **2** and **3** are accessible as supplementary material in Tables VI and VII, respectively. Specific rate constants are calculated on the basis of a reversible model, in which the equilibrium constant is also treated as a variable. Arrhenius and Eyring parameters are extracted in the conventional manner and are collected in Table III. To facilitate analysis, specific rate constants for all four compounds are calculated at the common temperature 160 °C and are collected in Table IV along with Eyring parameters and ratios of rate constants.

Pentaene **2** reacts 78 times slower than pentaene **3**. That a portion of the slowing originates in the difference in configuration is confirmed by the discovery that (*E*,*Z*)-**5** reacts 11 times slower than (*E*,*E*)-**5**, both of identical extensivity. After this configurational effect is factored, pentaene **2** is seen still to rearrange slower than **3** by a factor of 7.0. We propose provisionally that the origin of this further slowing lies in the operation of Kramers'

(15) Doering, W. von E.; Birladeanu, L. *J. Am. Chem. Soc.* **1986**, *108*, 7442–7444.

(16) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347–1353.

(17) But we note that, despite identical *levels* of substitution in **2** and **3**, *position* of substitution differs, particularly in respect to the theoretically potentially critical, central carbon atom in the corresponding pentadienyl radicals. These atoms are secondary in **2** and tertiary in **3**. Exploration of this point by comparison of the rates of rearrangement of the pentaenes derived, for example, from 1,5-dimethyl- and 1,7-dimethylbicyclo[4.4.0]-octa-4,6-dien-3-one has high priority.

(18) (a) *Steroid Reactions. An Outline for Organic Chemists*; Djerassi, C., Ed.; Holden Day: San Francisco, 1963; p 230.

(19) Ruzicka, L.; Plattner, Pl. A.; Furrer, M. *Helv. Chim. Acta* **1944**, *27*, 524–530.

Table III. Thermal syn-anti Isomerization of 3,3'-Bicholesta-4,6-dienylidene (**3**) and 2,2'-Bicholesta-3,5-dienylidene (**2**) in Benzene-d_6: Specific Rate and Equilibrium Constants and Activation Parameters

	3		**2**	
T (°C)[a]	$k_1(10^{-6}\ s^{-1})$[b]	K	$k_1(10^{-6}\ s^{-1})$[b]	K
110.9	0.984 ± 0.018[c]	0.649		
121.5	3.19 ± 0.03	0.655		
132.4	9.29 ± 0.11[d]	0.658		
145.0	28.9 ± 0.3	0.670		
154.2	75.4 ± 0.5	0.674		
165.5	198.0 ± 0.3	0.687		
169.1			3.77 ± 0.04	0.582
186.2			17.93 ± 0.20	0.593
196.5			43.1 ± 0.6	0.597
208.4			117.5 ± 1.5	0.609
Arrhenius Plot ($1/T$ vs log k)				
E_a (kcal/mol)	32.39 ± 0.36		36.98 ± 0.15	
log A	12.43 ± 0.19		12.85 ± 0.07	
Eyring Parameters				
$\Delta H^{\ddagger}$ (kcal/mol)	31.6[e]		36.1[f]	
$\Delta S^{\ddagger}$ (eu)	−4.3		−2.6	
Thermodynamics ($1/T$ vs log K)				
$\Delta\Delta H°$ (kcal/mol)	0.34 ± 0.04		0.48 ± 0.05	
$\Delta\Delta S°$ (eu)	0.01 ± 0.09		0.01 ± 0.11	

[a] ±0.2 °C. [b] Calculated by linear regression by using the usual expression for reversible first-order reactions: $k_1 + k_{-1} = (1/t)\ \ln[(x_{eq} - x_0)/(x_{eq} - x)]$; $K = k_1/k_{-1}$ = syn/anti. [c] Standard errors should be doubled for 90% confidence limits. [d] The 29 940 s point (Table VI, supplementary material) is omitted in the calculation. [e] Calculated at 138.2 °C. [f] Calculated at 188.8 °C.

Table IV. Summary of Specific Rate Constants and Eyring Parameters, Calculated at 160.0 °C from Arrhenius Parameters, for syn-anti Isomerization of (*E,E*)-**5**, (*E,Z*)-**5**, (*E,E*)-**3**, and (*E,Z*)-**2**[a]

reactant	k_1[b]	k_E/k_Z	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
(*E,E*)-**5**	63.2[c]	11.1	32.1	−4.4
(*E,Z*)-**5**	5.71[d]		34.0	−4.8
(*E,E*)-**3**	121.3[e]	77.8	31.6	−4.3
(*E,Z*)-**2**	1.56[e]		36.1	−2.6

[a] $k_{(E,Z)\text{-}5}/k_{(E,Z)\text{-}2} = 3.66$; $[k_{(E,E)\text{-}3}/k_{(E,Z)\text{-}2}]/[k_{(E,E)\text{-}5}/[k_{(E,Z)\text{-}5}] = 7.03$; $k_{(E,E)\text{-}5}/k_{(E,E)\text{-}3} = 0.52$. [b] In units of $10^{-6}\ s^{-1}$. [c] Calculated from the mean Arrhenius parameters of Table IV, ref 1. [d] Calculated from Arrhenius parameters in Table II. [e] Calculated from the Arrhenius parameters in Table III.

solvent friction[3] as a dynamic, solvent-induced impediment to internal rotation. Its magnitude is thought to depend on the extent of penetration of the rotating component into the domain of the solvent. It should be noted that a "static" solvent effect cannot be excluded.[4d]

The Eyring parameters in Table IV confirm that the configurational and extensivity factors are both associated with enthalpy of activation rather than entropy of activation. In the compounds examined here, 2.6 kcal/mol appears to be allocable to solvent friction and 1.9 kcal/mol to the configurational factor.

How solvent friction should be related quantitatively to the ratio of the extensivity of **2** and **3** is not clear, but at this stage of exploration, the qualitative reality of the concept is probably the more important consideration. By a simple count of the level of carbon extensions from the axis of rotation, **3** has an extensivity of 2 and **2** an extensivity of 5 at the least and 7 at the most. The goal is translation of solvent swept aside into a correction that could be applied to the observed enthalpy of activation and emerge with an improved approximation to the experimentally inaccessible gas-phase enthalpies of activation.

The operation of solvent friction would imply a correlation between rate and viscosity. At atmospheric pressure and the temperatures at which pentaenes **2** and **3** rearrange, viscosities of a wide range of solvents are all low and about equal, but they can be raised dramatically by increasing pressure. Unfortunately, such efforts undertaken in collaboration with Professor F.-G. Klärner, Ruhr-Universität, Bochum, have been frustrated by an extreme tendency of **3** to polymerize at high pressures.

This work, we hope, will encourage further experimentation directed toward the evaluation of extensivity and solvent friction as a factor affecting rates in solution.

Experimental Section

General Procedure. Unless explicitly noted ("300 MHz" refers to a Bruker AM-300 instrument), ^1H and ^{13}C NMR spectra are measured in $CDCl_3$ solution on a Bruker AM-500 instrument. Spin-lattice relaxation times (T_1's) are determined by the inversion recovery method with use of vacuum-sealed solutions in $CDCl_3$ or C_6H_6. All chemical shifts are reported in parts per million (δ) from TMS.

Infrared spectra are recorded on a Perkin-Elmer Model 337 grating spectrophotometer and reported in inverse centimeters. Liquid samples are observed as thin films on a NaCl plate, whereas solid samples are measured as thin layers prepared by evaporating $CHCl_3$ solutions on a NaCl plate.

UV-visible electronic spectra are determined with a Varian Cary 219 or 2390 spectrophotometer in spectrograde hexanes and are reported as λ_{max} in nanometers.

4,6,7,8-Tetrahydro-2(3*H*)-naphthalenone. This ketone is synthesized by the method of Gaidamovich and Torgov.[14] 6-Methoxy-1-tetralone (25.1 g, 0.142 mol) is reduced by sodium (28.1 g) and ethanol (120 mL) in liquid ammonia (800 mL). Conventional workup gives practically pure 1,2,3,4,5,8-hexahydro-1-hydroxy-6-methoxynaphthalene (23.1 g), which is dissolved in ether (400 mL) and dehydrated by stirring with 10% HCl (200 mL) at room temperature for 2 h. Distillation of the crude product affords 13.5 g (64% overall yield) of colorless liquid: bp 102–112 °C (1.8 mmHg) [lit.[14] bp 74–75 °C (1.2 mmHg)]; ^1H NMR (300 MHz) 6.07 (m, 1 H), 5.74 (s, 1 H), 2.64 (t, 2 H, J = 7.4 Hz), 2.51–2.42 (m, 4 H), 2.27 (m, 2 H), 1.79 (q, 2 H, J = 6.4 Hz); IR 2940, 1665, 1636, 1593, 1440, 1340, 1259, 1204, 1190, 930, 896, 810.

4,4',6,6',7,7',8,8'-Octahydro-2,2'-bi-3*H*-naphthylidene ((*E,Z*)-5). 4,6,7,8-Tetrahydro-2(3*H*)-naphthalenone (12.0 g, 81.0 mmol) in THF (30 mL) is added to "Titanium Reagent"[1] [from 23.0 g (121 mmol) of $TiCl_4$, 15.9 g (243 mmol) of activated zinc dust, and 6.6 mL of pyridine in THF (300 mL)] and stirred at room temperature for 15 min. The crude product is dissolved in 200 mL of CH_2Cl_2–petroleum ether (1:3) and passed through a silica gel column, which is eluted with 300 mL of the same solvent. Removal of solvent in vacuo gives a mixture (5.7 g) of *anti*-(*E,Z*)-**5** and *syn*-(*E,Z*)-**5** in a ratio, 82:12, from which *anti*-(*E,Z*)-**5** is isolated as yellow crystals by recrystallization twice from THF at −78 and −20 °C: mp 125–126.5 °C (in evacuated sealed tube); ^1H NMR (C_6D_6, assignments based on decoupling experiments) 6.36 (s, 2 H, H-1,1'), 5.48 (m, 2 H, H-5,5'), 2.56 (t, 4 H, J = 6.8 Hz, H-3,3'), 2.35 (m, 8 H, H-4,4' and H-8,8'), 2.05 (m, 4 H, H-6,6'), 1.65 (quintet, 4 H, J = 6.2 Hz, H-7,7'); ^{13}C NMR 135.4 (s), 134.5 (s), 128.8 (s), 123.6 (d), 121.6 (d) 31.3 (t), 30.3 (t), 26.1 (t), 25.7 (t), 23.4 (t); IR 2938, 2888, 2826, 1430, 988, 884, 864, 794; UV-vis 333 sh (46 700), 348 (57 500), 366 (47 000).

Two recrystallizations of the concentrated mother liquors from CH_2Cl_2 at −78 °C afford pure *syn*-(*E,Z*)-**5** as light yellow crystals: mp 93.5–94.5 °C (in evacuated sealed tube); ^1H NMR (C_6H_6, assignments based on decoupling experiments) 6.63 (s, 2 H, H-1,1'), 5.48 (m, 2 H, H-5,5'), 2.43 (t, 4 H, J = 6.7 Hz, H-3,3'), 2.34 (m, 8 H, H-4,4' and H-8,8'), 2.05 (m, 4 H, H-6,6'), 1.64 (q, 4 H, J = 6.2 Hz, H-7,7'); ^{13}C NMR 134.8 (s), 134.4 (s), 129.0 (s), 123.5 (d), 120.3 (d), 31.2 (t), 30.3 (t), 26.4 (t), 26.2 (t), 23.4 (t); IR 2926, 2826, 1435, 1140, 1002, 987, 931, 880, 860, 792, 740, 658; UV-vis 326 sh (41 000), 340 (53 700), 356 (41 800).

All samples of (*E,Z*)-**5** are stored in the dark at −20 °C under vacuum to retard polymerization.

Nuclear Overhauser enhancements are determined by the gated decoupling method by using degassed solutions in C_6D_6 and a relaxation delay and a saturation period between pulses 5 times the longest T_1's of the concerned protons. *anti*-(*E,Z*)-**5**: H-1 (6.36) [H-3 (2.56) saturated], 28.3%; H-3 [H-1 saturated], 9.7%. *syn*-(*E,Z*)-**5**: H-1 (6.63) [H-3 (2.43) saturated], 2.3%; H-3 [H-1 saturated], 0.6%.

Kinetics of syn–anti Isomerization of (*E,Z*)-5. Ampules of solutions (0.35 mL) of a mixture of *anti*-(*E,Z*)-**5** (1.4–2.0% w/v) in C_6D_6 containing diglyme (0.29% v/v) as internal standard are prepared and heated in the manner previously described.[1] The resulting mixtures of *anti*-(*E,Z*)-**5** and *syn*-(*E,Z*)-**5** are analyzed on a Bruker AM-300 instrument by integrating H-1 signals at 6.36 (*anti*-(*E,Z*)-**5**, T_1 = 0.94 ± 0.07 s) and 6.63 (*syn*-(*E,Z*)-**5**, T_1 = 1.08 ± 0.07 s). A relaxation delay and a saturation period 4 and 3 times the longest T_1's, respectively, of the concerned protons are taken between pulses. Approximately 100 scans are collected with 10° pulses and a pulse interval of 8.0 s, which is longer than the T_1's of these protons. This pulse interval is found to be also long enough to

integrate quantitatively (error <1%) the methyl (3.34, T_1 = 9.02 ± 0.36 s) and the two methylene signals of diglyme, which are used for calculation of recoveries.

Correction is needed in the ratio of *anti*- to *syn*-(*E*,*Z*)-**5** because one of the ^{13}C satellite peaks of H-1 of *anti*-(*E*,*Z*)-**5** overlaps the H-1 of *syn*-(*E*,*Z*)-**5** and that of H-1 of *syn*-(*E*,*Z*)-**5** overlaps H-1 of *anti*-(*E*,*Z*)-**5**. Because the natural abundance of ^{13}C is 1.10%, the molar ratio of *anti*-(*E*,*Z*)-**5** and *syn*-(*E*,*Z*)-**5** can be determined by the following equations:

$$\text{anti (\%)} = (98.90A_{\text{anti}} - 0.55A_{\text{syn}})/(98.90 - 0.55)$$

$$\text{syn (\%)} = (98.90A_{\text{syn}} - 0.55A_{\text{anti}})/(98.90 - 0.55)$$

where A_{anti} and A_{syn} are the areas (%) of H-1 of *anti*-(*E*,*Z*)-**5** and H-1 of *syn*-(*E*,*Z*)-**5** determined by integration, respectively.

The resulting data are recorded in Table V and relegated to supplementary material. Rate and equilibrium constants are optimized simultaneously by the nonlinear least-squares method to fit the reversible first-order, kinetic equation to the observed data. Results are given in Table II.

Cholesta-3,5-dien-2-one. This compound is prepared from cholest-4-en-3-one (Aldrich Chemical, mp 79–81 °C) by the sequence of reactions outlined in Scheme V. The first step involves a Shapiro reaction,[20] in which a solution of the tosylhydrazone[21] of cholest-4-en-3-one (9.8 g, 17.7 mmol) in dry THF (240 mL) is treated under argon with methyllithium (42.5 mmol; 31 mL of a 1.4 M solution in ether) at 16–18 °C (cooling by ice bath) over a period of 35 min. Stirring is continued for an additional 2 h. The reaction mixture is quenched with 20 mL of water and freed of THF in vacuo. A solution of the residue in methylene chloride is washed with water, dried over $MgSO_4$, filtered through silica gel, and concentrated to give 3.9 g (60% of theoretical yield) of cholesta-2,4-diene: mp 67.5-68 °C (lit.[22] mp 68.5 °C); ^1H NMR 5.78–5.73 (m, 1 H), 5.65–5.58 (m, 1 H), 2.4–0.7 (complex m, 39 H).

A stirred solution of 3.9 g of the diene, used without further purification, in 985 mL of methylene chloride and 225 mL of methanol containing 40 mg of Rose Bengal, and with a stream of oxygen passing through, is cooled to −20 °C and irradiated for 35 min with two General Electric RS 275-W sun lamps. Removal of solvent in vacuo gives a residue that is flash chromatographed on silica gel: Elution with hexane gives 0.82 g of recovered diene; elution with 5% ethyl acetate–hexane affords 2.55 g (76% of theoretical yield) of 2,5-peroxidocholest-3-ene: mp 112-112.5 °C (lit.[22] mp 113–114 °C); ^1H NMR 6.53 (dd, 1 H, J = 10 Hz, J = 8 Hz), 6.6 (d, J = 10 Hz), 2.1–0.6 (complex m, 41 H).

A solution of 2.55 g of this peroxide in 90 mL of THF containing 5% water is added to 1.2 g of aluminum amalgam[23] in 500 mL of THF containing 1% water cooled in an ice bath. After being stirred for 40 min, the reaction mixture is filtered through Celite and concentrated in vacuo. Flash chromatography on silica gel (40% ethyl acetate–hexane) gives 1.85 g (73% of theoretical yield) of 2,5-dihydroxycholest-3-ene: after one crystallization from methanol, mp 155–155.5 °C; ^1H NMR 5.75 (d, 1 H, J = 10 Hz), 5.65 (d, 1 H, J = 10 Hz), 4.28 (br s, 1 H), 2.1–0.6 (complex m, 41 H).

Treatment of this diol (0.78 g) with 20 mL of acetic anhydride under argon at 110 °C for 1 h gives a reaction mixture, from which crystals separate on cooling. Recrystallization from acetone gives 0.6 g (73% of theoretical yield) of 2-acetoxy-5-hydroxycholest-3-ene: mp 128.5-129 °C; ^1H NMR 5.80 (d, 1 H, J = 10.2 Hz), 5.65 (d, 1 H, J = 10.2 Hz), 5.4 (br s, 1 H), 2.1–0.6 (complex m, 41 H).

To a stirred solution of thionyl chloride (47.6 mg, purified by distillation from dipentene–linseed oil) and 98 mg of 4-(dimethylamino)-pyridine in methylene chloride (4 mL) at 0 °C under argon, a solution of the acetoxy hydroxy derivative above (85 mg, 2 mmol) in 4 mL of methylene chloride is added. After being stirred at 0 °C for 1 h, the reaction mixture is poured over ice-cold 5% aqueous $NaHCO_3$. The separated organic layer is washed with water, dried over $MgSO_4$, and concentrated in vacuo to a residue, which upon flash chromatography on silica gel (5% ethyl acetate–hexane) gives 20 mg (24.7% of theoroetical yield) of 2-acetoxycholesta-3,5-diene: ^1H NMR 6.03 (d, 1 H, J = 9.8 Hz), 5.55 (br s, 1 H), 5.47 (d, 1 H, J = 9.8 Hz), 2.15 (s, 3 H), 2.1–0.6 (complex m, 39 H).

Hydrolysis of the acetate (60 mg, 0.15 mmol) is effected by treatment with solid potassium carbonate (312 mg) in methanol (20 mL) at 0 °C. After being stirred for 90 min under argon, the reaction mixture is filtered to remove unused K_2CO_3, concentrated in vacuo, and treated with water. A solution of the resulting precipitate in methylene chloride is dried over $MgSO_4$ and concentrated to a residue (50 mg) of 2-hydroxycholesta-3,5-diene, which is used in the following step with no further purification: ^1H NMR 5.95 (d, 1 H, J = 9.75 Hz), 5.57 (d, 1 H, J = 9.75 Hz), 5.52 (br s, 1 H), 4.35 (br s, 1 H), 2.3–0.7 (complex m, 39 H).

Oxidation of the dienol (50 mg, 0.13 mmol) in 3 mL of methylene chloride is effected by treatment with periodinane, the Dess–Martin reagent,[24] (120 mg) in 3 mL of methylene chloride under argon for 7 min at room temperature. After the addition of 10 mL of ether, the mixture is stirred at 0 °C with 3 mL of 0.01 M aqueous KOH for 10 min. The organic layer is extracted with 3 mL of 0.01 M aqueous KOH, washed twice each with 3 mL of water, dried over $MgSO_4$, and concentrated in vacuo. A solution of the residue in methylene chloride is filtered through silica gel, washed with 5 mL of 25:75 ethyl acetate–hexane. Removal of solvent in vacuo leaves 46 mg of cholesta-3,5-dien-2-one, used in the next step without further purification: after two recrystallizations from methanol, mp 121.5–122 °C (lit.[19] mp 121.5–122.5 °C); ^1H NMR 6.88 (d, 1 H-4, J = 9.8 Hz), 6.03 (dd, 1 H-6, J = 3.25 Hz, J' = 4.70 Hz), 5.82 (d, 1 H-3, J = 9.8 Hz), 2.53 (d, 1 H-1, J = 15.5 Hz), 2.31 (dt, 1 H-7, J = 14.6 Hz, J' = 5.4 Hz), 2.21 (d, 1 H-1, J = 15.5 Hz), 2.04 (dt, 1 H-7, J = 12.7, J = 3.5 Hz), 1.90–1.72 (m, 2 H), 1.66–0.95 (complex m), 1.06 (s, 3 H, Me-19), 0.90 (d, 3 H, Me-21, J = 6.5 Hz), 0.85 (d, 6 H, Me-26, Me-27, J = 3.5 Hz), 0.70 (s, 3 H, Me-18); IR (film) 1680.

2,2'-Bicholesta-3,5-dienylidene (2). Reductive coupling of cholesta-3,5-dien-2-one is accomplished by the Mukaiyama-Tyrlik-McMurry reaction[9] closely following the procedure of Lenoir.[1,13] Activated zinc dust (240 mg, 3.67 mmol) and pyridine (0.12 mL) are added slowly from the bent tube to a solution of $TiCl_4$ (0.20 mL, 1.8 mmol) in THF (5 mL), freshly distilled from $LiAlH_4$, under argon at 0 °C with stirring. At room temperature, this mixture is treated with a solution of the dienone (24.7 mg, 0.065 mmol) in dry THF (1 mL) and stirred for 20 more min, after which starting material is shown by TLC (silica gel eluted with 1:9 ethyl acetate–hexane) to be completely reacted. Quenching with 10% aqueous HCl (30 mL) and three extractions with methylene chloride (30 mL each) afford an extract, which is washed with 10% aqueous sodium carbonate (50 mL) and with saturated aqueous NaCl (50 mL), dried over $MgSO_4$, and concentrated to a residue (28 mg), which is subjected to flash chromatography on silica gel. Elution with hexane affords 3 mg (12% of theoretical yield) of **2** consisting of pale yellow crystals of a mixture of *syn*- and *anti*-**2** in the ratio 66:34: ^1H NMR (C_6D_6) 6.74 (d, 2 H, *syn*-H-3,3', J = 9.9 Hz), 6.61 (d, 2 H, *anti*-H-3,3', J = 10.0 Hz), 6.19 (d, 2 H, *anti*-H-4,4', J = 10.0 Hz), 6.11 (d, 2 H, *syn*-H-4,4', J = 9.9 Hz), 5.62-5.56 (m, 2 H, H-6,6'), 3.01 (d, 2 H, *syn*-H-1, J = 15.8 Hz), 2.96 (d, 2 H, *anti*-H-1, J = 15.8 Hz), 2.20–2.12 (m, 2 H), 2.08–1.97 (m, 2 H), 1.92–1.82 (m, 2 H), 1.76–0.56 (complex m), 1.10 (s, 6 H, Me-19), 1.05 (d, 6 H, *syn*-Me-21, J = 5.4 Hz), 1.03 (d, 6 H, *anti*-Me-21, J = 5.4 Hz), 0.94 (d, 12 H, Me-26, Me-27, J = 5.4 Hz), 0.69 (s, 6 H, Me-21).

Cholesta-4,6-dien-3-one. A reaction mixture, obtained by the addition of cholest-4-en-3-one (4.25 g, 0.11 mmol) to a boiling solution of chloranil (6.0 g, 0.024 mmol) in *tert*-butyl alcohol (200 mL) and refluxing for 4.5 h, is cooled, filtered to remove unreacted chloranil, and concentrated under vacuum to afford a crude product, a chloroform solution of which is washed successively with water, 5% aqueous sodium hydroxide, and water until colorless, dried over $MgSO_4$, and concentrated to a residue. Purification by flash chromatography on neutral alumina followed by crystallization from ethanol affords 1.1 g (26% of theoretical yield) of cholesta-4,6-dien-3-one: mp 79–80 °C (lit.[25] mp 80.5–81.5 °C); ^1H NMR 6.13 (dd, 1 H, J = 9.8 Hz, J' = 1.6 Hz), 6.07 (dd, 1 H-7, J = 9.8 Hz, J' = 2.6 Hz), 5.65 (s, 1 H-4), 2.60–2.55 (m, 1 H, H-2), 2.46–2.37 (m, 1 H, H-2), 2.18 (t, 1 H, H-8, J = 10.2 Hz), 2.05 (dt, 1 H, H-1, J= 12.9 Hz, J' = 2.6 Hz), 2.02–1.95 (m, 1 H, H-1), 1.94-1.84 (m, 1 H, H-9), 1.82–1.74 (m, 1 H), 1.74–1.66 (dt, 1 H, J = 13.8 Hz, J' = 5.0 Hz), 1.55–0.96 (complex m), 1.09 (s, 3 H, Me-19), 0.1 (d, 3 H, Me-21, J = 6.5 Hz), 0.87 (d, 3 H, Me-26 (or 27), J = 2.3 Hz), 0.84 (d, 3 H, Me-27 (or 26), J = 2.3 Hz), 0.74 (s, 3 H, Me-18).

3,3'-Bicholesta-4,6-dienylidene (3). Application of the Mukaiyama–Tyrlik–McMurry procedure, as described above, to cholesta-4,6-dien-3-one (264 mg), $TiCl_4$ (0.4 mL), zinc (480 mg), and pyridine (0.24 mL) in THF (10 mL) affords, after flash chromatography on silica gel (hexane), 3,3'-bicholesta-4,6-dienylidene (**3**) as a mixture of *syn*- and *anti*-**3**: 77 mg, 29% of theoretical yield; MS *m/e* 732; ^1H NMR 6.45 (s, 2 H, *syn*-H-4,4'), 6.25 (s, 2 H, *anti*-H-4,4'), 6.04-6.05 (dd, 2 H, *syn*/*anti*-H-6,6', J = 9.8 Hz), 5.66 (m, 2 H, *syn*/*anti*-H-7,7'), 2.78 (d, 2 H, *anti*-H-2,2', J = 15.9 Hz), 2.51 (d, 2 H, *syn*-H-2,2', J = 15.9 Hz),

(20) Shapiro, R. H. *Org. React.* (*N.Y.*) **1976**, *23*, 405–507.
(21) Kabalka, G. W.; Hutchins, R.; Natale, N. R.; Yang, T. C.; Broach, V. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 293.
(22) Skau, E. L.; Bergmann, W. *J. Org. Chem.* **1938**, *3*, 166–174.
(23) Ferris J. P.; Sanchez, R. A.; Mancuso, R. W. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 32–35.
(24) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156–4158.
(25) Wilds, A. L.; Djerassi, C. *J. Am. Chem. Soc.* **1946**, *68*, 1712–1715.

2.45-2.26 (m, 2 H), 2.14 (pseudo t, 2 H, J = 9.0 Hz), 2.02 (d, 2 H, J = 21 Hz), 1.83-1.70 (m, 6 H), 1.60-0.96 (complex m), 0.95 (s, 6 H, Me-19,19'), 0.92 (d, 6 H, Me-21,21', J = 5.4 Hz), 0.87 (d, 12 H, Me-26,26', Me-27,27', J = 6.6 Hz), 0.74 (s, 6 H, Me-21,21').

Kinetics of syn-anti Rearrangement of 2 and 3. Kinetics are carried out as described above. The resulting data for **2** and **3** are given in Tables VI and VII, respectively, as supplementary material.

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Supplementary Material Available: Unprocessed kinetic data for the thermal rearrangements of *anti*-(*E*,*Z*)-**5** (Table V), *syn*-(*E*,*Z*)-**2** (Table VI), and *syn*-(*E*,*Z*)-**3** (Table VII) (4 pages). Ordering information is given on any current masthead page.

Central and Lateral Bicyclo[1.1.0]butane Bond Cleavage with Subsequent Wagner-Meerwein Rearrangements or Carbene Formation in the 185-nm Photolysis of Tricyclo[3.1.0.0^{2,6}]hexane, Tricyclo[4.1.0.0^{2,7}]heptane, and Tricyclo[5.1.0.0^{2,8}]octane

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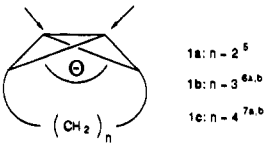
Abstract: The 185-nm photochemistry of tricyclo[3.1.0.0^{2,6}]hexane, tricyclo[4.1.0.0^{2,7}]heptane, [1,7-d_2]tricyclo[4.1.0.0^{2,7}]heptane, tricyclo[5.1.0.0^{2,8}]octane, and [1-d]tricyclo[5.1.0.0^{2,8}]octane was investigated. Tricyclo[5.1.0.0^{2,8}]octane yields bicyclo[4.2.0]oct-7-ene, tricyclo[4.1.0.0^{2,7}]heptane yields 85% bicyclo[3.2.0]hept-6-ene and 15% 3-methylenecyclohexene, and tricyclo[3.1.0.0^{2,6}]hexane yields 39% 3-methylenecyclopentene, 15% 1,3-cyclohexadiene, 26% *trans*-1,3,5-hexatriene, and 20% *cis*-1,3,5-hexatriene. From the deuterium-labeling studies, it is concluded that, in the case of the tricyclooctane, the central bicyclobutane bonds cleave in the primary step to give radical cationic or zwitterionic species that undergo a Wagner-Meerwein rearrangement. Also, in the case of tricycloheptane, this is the dominating pathway but lateral C-C bond cleavage with subsequent carbene and product formation takes place to the extent of ca. 15%. For tricyclohexane, this pathway becomes the major route. Our photomechanistic observations are in good agreement with earlier theoretical investigations on the relative energetic ordering of the bicyclobutane HOMOs, in that the product composition reflects this.

Photolysis of organic substrates at 185 nm in solution has become a well-established photochemical method in recent years.[1a-f] An important result is that the concept of orbital symmetry conservation[2] cannot be applied without some restrictions on the electrocyclic ring opening of alkyl-substituted cyclobutenes.[3a-c] It was shown that the diene products were not generated in the expected disrotatory manner.[3b,c] Besides π,π^* excited states, also radical cation like (π,3s) Rydberg states play an important role.[3a-c] Dunkin and Andrews[4] have developed an orbital symmetry concept in which preferential conrotatory ring opening of the cyclobutene radical cation in its ground state was predicted. The existence of such an additional intermediate could explain the observed lack of stereoselectivity.

Further information on ring-opening processes of small strained molecules, which only absorb $\lambda \leq 254$ nm radiation, should be accessible by studying the 185-nm photolysis of the bridged bicyclo[1.1.0]butanes **1a-c**. All of these compounds are literature known, and they can be deuterated or alkylated at the bridgehead



positions of the central carbon-carbon bond, thereby providing a stereolabel for mechanistic purposes. The following questions were of interest in regard to the 185-nm photochemistry of the bridged bicyclo[1.1.0]butanes **1a-c**:

Do such photolyses take a mechanistically uniform course for the different length (n = 2-4) of the connecting bridge in **1a-c**?

Does one observe changes in the ring-opening propensity of the central and lateral carbon-carbon bonds as a function of the dihedral angle θ?

Does one observe diradical chemistry or do radical cation like Rydberg states or zwitterions intervene that can be recognized by typical Wagner-Meerwein rearrangements or by trapping with

(1) (a) von Sonntag, C.; Schuchmann, H.-P. *Adv. Photochem.* **1977**, *10*, 59. (b) Dorofeev, Y. I.; Skurat, V. E. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 527. (c) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1984**, *5*, 57. (d) Adam, W.; Oppenländer, T. *Angew. Chem.* **1986**, *98*, 659. (e) Leigh, W. J.; Srinivasan, R. *Acc. Chem. Res.* **1987**, *20*, 107. (f) Steinmetz, M. G. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York/Basel, 1987; Vol. 8, p 67.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797.

(3) (a) Adam, W.; Oppenländer, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921. (b) Clark, K. B.; Leigh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 6086. (c) Dauben, W. G.; Haubrich, J. E. *J. Org. Chem.* **1988**, *53*, 600.

(4) Dunkin, I. R.; Andrews, L. *Tetrahedron* **1985**, *41*, 145.

(5) Christl, M.; Brüntrup, G. *Chem. Ber.* **1974**, *107*, 3908.

(6) (a) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019. (b) Gassman, P. G.; Richmond, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2090.

(7) (a) Düker, A. Ph.D. Thesis, Ludwig-Maximilians-Universität München, 1986. (b) Christl, M.; Herzog, C.; Kemmer, P. *Chem. Ber.* **1986**, *119*, 3045.

0002-7863/91/1513-4563$02.50/0