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Dependence of Stabilization Energy of an (*E*,*Z*)-Pentadienyl Radical on Substitution. Role of "Solvent Friction": Negligible at Higher Temperatures?

W. von E. Doering,* Yi-qun Shi, and Da-chuan Zhao

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138-2902. *Received June 22, 1992*

Abstract: Pentaene **6** has the same configuration and degree of substitution as the previously reported pentaene, 2,2′-bicholestadienylidene **2**, and is thus a more suitable model of low extensivity for comparison with **2** of much higher extensivity. The rates of their thermal anti–syn rearrangements and derived Arrhenius parameters are essentially identical. The previous, tentatively proffered suggestion that solvent friction might have been responsible for the otherwise inexplicably slower rate of thermal cis–trans isomerization of **2** relative to compound **4** is no longer warranted. Instead it now appears that the enthalpy of stabilization in the pentadienyl radical is sensitive to substitution, at least at its central carbon atom, contrary to the earlier assumption based on the apparent insensitivity of the allyl radical to substitution.

In a recent exploration of the possible influence of "solvent friction", the rate of thermal anti–syn rearrangement of a "cylindrical" pentaene of low extensivity, **1**, was found to be 78 times faster than that of a paddle-like pentaene of high extensivity, **2** (see Chart I and Table IV).[1] Had the two compounds differed in no other significant way but extensivity, interpretation in terms of degree of extension into the solvent would have been relatively straightforward. As the choice of **1** and **2** as test compounds had been based mainly on the relatively facile accessibility of the latter, the two compounds by happenstance also differed in configuration and degree of substitution (see Chart I). Configuration having been surmised to be the more significant factor, two simpler model compounds, **3** and **4**, both of low extensivity and nearly identical patterns of substitution, were examined. Compound **4** of (*E*,*Z*) configuration indeed underwent cis–trans isomerization more slowly than compound **3** of (*E*,*E*) configuration by a factor of 11. Although configuration had now been shown to be an important factor in the stabilization energy of the pentadienyl radical, solvent friction appeared to remain as a small but significant factor; that is, extensivity in compound **2** appeared to have retarded the rate of rearrangement by the remaining factor of 7 (78:11). This latter conclusion, however, was deemed tentative owing to its dependence on the correctness of an assumption that the tertiary nature of C5 (steroid numbering; corresponding to the central carbon atom in the pentadienyl radical) in **1** compared with its secondary nature in **2** had been without effect. Support for this assumption was entirely indirect, for it came from studies of the allyl radical which had revealed no experimentally significant dependence of enthalpy of stabilization on degree of substitution by methyl groups.[1,2]

To place the possible role of solvent friction in these thermal rearrangements on more solid footing, direct examination of the effect of substitution by alkyl on the pentadienyl radical was needed. Compound **6** (see Chart II) was selected as superior to the originally selected compound **4** because **6** and **2** had identical configurations and patterns of substitution and differed only in extensivity. But compound **6** also has a quaternary methyl group in the position corresponding to C10 in **2** and **1**. To confirm that the effect of this methyl group was negligible, pentaene **5** was also included as a control for comparison with **3**. For good measure, triene **8** corresponding to **7** was also examined. The various compounds noted are shown in Chart II.

Triene **8** and polyenes **5** and **6** are synthesized by reductive coupling of the apposite ketones, **9**, **10**, and **11**, respectively, according to McMurry–Mukayama–Tyrlik (see Scheme I), as previously elaborated.[3] Ketone **9**, prepared following the procedure of Marshall and Fanta,[4] is converted to ketone **10** by the procedure of Banerjee and Angadi.[5] The ketonic precursor **11**

Chart I

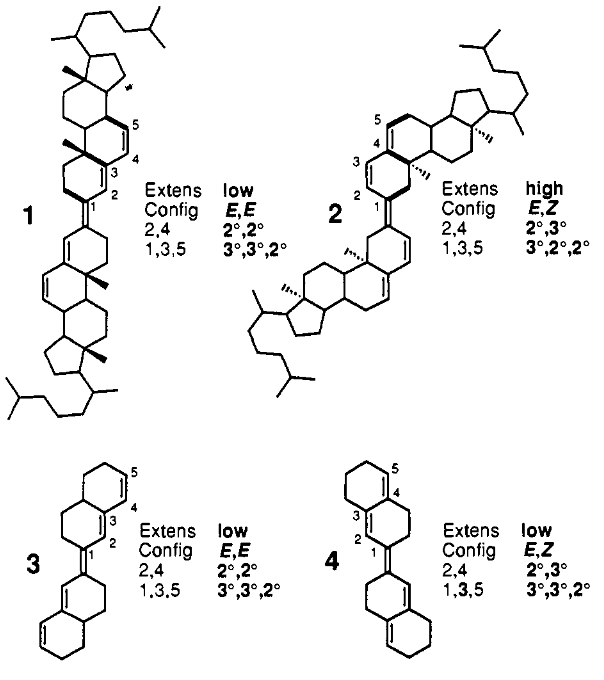
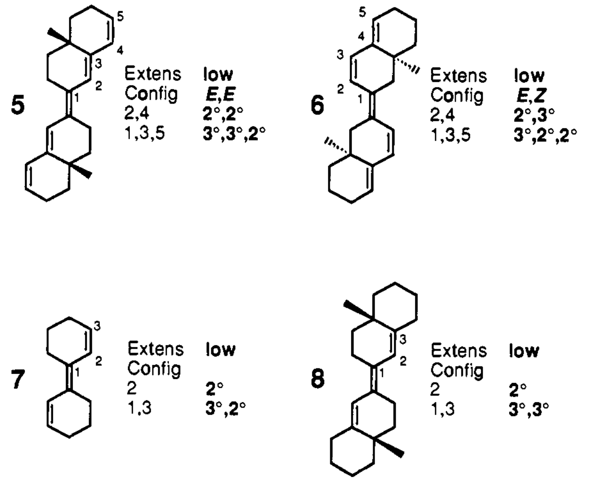


Chart II



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[1] Doering, W. v. E.; Birladeanu, L.; Cheng, X.-h.; Kitagawa, T.; Sarma, K. *J. Am. Chem. Soc.* **1991**, *113*, 4558–4563.

[2] Bauer, L. Bildungsenthalpie substituierter Allyl-Radikale (Enthalpy of Formation of Substituted Allyl Radicals). Ph.D. Dissertation, Ruhr-Universität, Bochum, Germany, 1991.

0002-7863/92/1514-10763$03.00/0

Scheme I

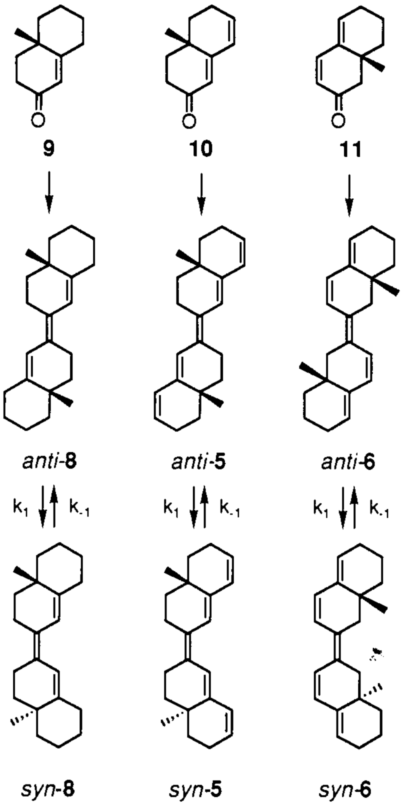

Table I. Thermal Isomerization of *syn*-**8** to *anti*-**8** in Benzene-d_6: Specific Rate and Equilibrium Constants and Activation Parameters

T, °C	k_1 ($\times10^{-6}$ s^{-1})[a]	K
207.7 ± 0.1	1.048 ± 0.02[b]	1.4018
235.7 ± 0.2	10.73 ± 0.1	1.3726
258.7 ± 0.1	62.5 ± 2.1	1.3436

Arrhenius plot [$1/T$ vs log k]
E_a = 40.64 ± 0.24 kcal/mol
log A = 12.49 ± 0.10
Eyring parameters[c]
$\Delta H^{\ddagger}$ = 39.6 ± 0.2 kcal/mol
$\Delta S^{\ddagger}$ = −4.4 ± 0.5 eu
thermodynamics [$1/T$ vs log K]
ΔH° = −0.41 ± 0.04 kcal/mol
ΔS° = −0.17 ± 0.08 eu

[a] Calculated by linear regression using the usual expression for reversible first-order reaction ($k_1 + k_{-1}$) = ($1/t$) ln [($X_{eq} - X_0$)/($X_{eq} - X$)]; $K = k_1/k_{-1}$. [b] Double all standard errors for 90% confidence limits. [c] Calculated at 233.2 °C.

of critical pentaene **6** is prepared following the procedure of Sims.[6]

The reversible, thermal, anti–syn configurational isomerizations are conducted in perdeuteriobenzene according to a previously published procedure.[1,3] The data relating concentration, time, and temperature are offered as supplementary material in Tables S1 (**8**), S2 (**5**), and S3 (**6**). Derived first-order rate constants and Arrhenius parameters are given in Tables I (**8**), II (**5**), and III (**6**), respectively. A summary of all results is given in Table IV.

In the present discussion, Eyring parameters refer to the rearrangement of anti isomer to syn, whence the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for **8** in Table I differ from those in Table IV by the values of ΔH° and ΔS°. Comparison of **7**[3,7] and **8** reveals no significant effect of either alkyl substitution or a greater number of extraneous atoms, including the bridgehead methyl group, on enthalpy and entropy of activation.[8] Similarly, comparison of **3** and **5** (Charts I and II) confirms that the bridgehead methyl group is an insignificant perturbation. A reassuring similarity in rates and activation parameters among **1**, **3**, and **5** is seen in Table IV!

Table II. Thermal Isomerization of α- and β-*anti*-**5** to α- and β-*syn*-**5** in Benzene-d_6: Specific Rate and Equilibrium Constants and Activation Parameters

T, °C	k_1 ($\times10^{-6}$ s^{-1})[a]	K
132.2 ± 0.2	7.56 ± 0.74[b]	0.571
154.2 ± 0.2	61.1 ± 2.1	0.582
164.2 ± 0.3	156.0 ± 6.1	0.591

Arrhenius plot [$1/T$ vs log k]
E_a = 33.2 ± 0.5 kcal/mol
log A = 12.78 ± 0.25
Eyring parameters[c]
$\Delta H^{\ddagger}$ = 32.4 ± 0.5 kcal/mol
$\Delta S^{\ddagger}$ = −2.7 ± 1.1 eu
thermodynamics [$1/T$ vs log K]
ΔH° = 0.34 ± 0.14 kcal/mol
ΔS° = −0.27 ± 0.32 eu

[a] Calculated by linear regression using the usual expression for reversible first-order reaction: ($k_1 + k_{-1}$) = ($1/t$) ln [($X_{eq} - X_0$)/($X_{eq} - X$)]; $K = k_{-1}/k_1$. [b] Double all standard errors for 90% confidence limits. [c] Calculated at 148.2 °C.

Table III. Thermal Isomerization of α- and β-*anti*-**6** to α- and β-*syn*-6 in Benzene-d_6: Specific Rate and Equilibrium Constants and Activation Parameters

T, °C	k_1 ($\times10^{-6}$ s^{-1})[a]	K
165.2 ± 0.2	2.29 ± 0.06[b]	0.763
184.7 ± 0.3	12.90 ± 0.22	0.768
195.9 ± 0.2	36.27 ± 0.94	0.781
208.6 ± 0.3	100.1 ± 2.8	0.804

Arrhenius plot [$1/T$ vs log k]
E_a = 36.7 ± 0.5 kcal/mol
log A = 12.62 ± 0.25
Eyring parameters[c]
$\Delta H^{\ddagger}$ = 35.7 ± 0.5 kcal/mol
$\Delta S^{\ddagger}$ = −3.6 ± 1.1 eu
thermodynamics [$1/T$ vs log K]
ΔH° = 0.48 ± 0.15 kcal/mol
ΔS° = −0.55 ± 0.34 eu

[a] Calculated by linear regression using the usual expression for reversible first-order reaction: ($k_1 + k_{-1}$) = ($1/t$) ln [($X_{eq} - X_0$)/($X_{eq} - X$)]; $K = k_1/s$. [b] Double all standard errors for 90% confidence limits. [c] Calculated at 186.9 °C.

The datum relating to **6** had been expected to confirm the assumption made earlier[1] that the different degree of substitution at the central carbon atoms in the pentadienyl radicals comprising the 90° transition states, tertiary in **4**, but secondary in **6**, would have no effect. The two were expected to be kinetically indistinguishable, and **6** of low extensivity was expected to react faster than **2** of high extensivity. That this prediction has not been fulfilled belies the original assumption of insensitivity to substitution and removes support within experimental uncertainty for the earlier conclusion that extensivity might be a small but significant factor in these thermal rearrangements.[1]

Morawetz and his co-workers had arrived at the same conclusion as a result of their extensive comparison of reactions in polymers and small-molecule analogs for signs of the operation of solvent friction (extensivity).[9] They also provided decisive evidence that a crankshaft-like motion that was expected to

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[3] Doering, W. v. E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288–4297.

[4] Marshall, J. A.; Fanta, W. I. *J. Org. Chem.* **1964**, *29*, 2501–2505.

[5] Banerjee, D. K.; Angadi, V. B. *J. Org. Chem.* **1961**, *26*, 2988–2989.

[6] Sims, J. J. *J. Org. Chem.* **1967**, *32*, 1751–1754.

[7] Doering, W. v. E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461–1470.

[8] The 2 kcal/mol difference between the gas-phase value for **7**[7] and the solution value[3] is being reexamined as part of a study of the influence of change in phase on the rates and activation parameters of thermal rearrangements.

[9] (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.

Table IV. Activation Parameters and Specific Rate Constants at 165.85 °C (440 K) for Thermal Cis–Trans Isomerization about the Central Double Bond of Six Pentaenes, **1–6**, and Two Trienes, **7** and **8**

compd	T range, °C	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_1 \times 10^5$
1	110.9–165.5	32.4 ± 0.4	12.43 ± 0.19	31.6 ± 0.4	−4.3 ± 0.9	21.8
2	169.1–208.4	37.0 ± 0.2	12.85 ± 0.07	36.1 ± 0.2	−2.6 ± 0.3	0.30
3	121.2–166.8	32.9 ± 0.2	12.41 ± 0.26	32.1 ± 0.2	−4.4 ± 0.3	11.7
4	144.6–192.3	34.9 ± 0.3	12.35 ± 0.14	34.0 ± 0.3	−4.8 ± 0.7	1.04
5	132.2–164.2	33.2 ± 0.5	12.78 ± 0.26	32.4 ± 0.5	−2.7 ± 1.1	19.5
6	165.2–208.6	36.6 ± 0.5	12.62 ± 0.25	35.7 ± 0.5	−3.6 ± 1.1	0.55
7[a]	207.7–258.7	39.9 ± 0.6	12.14 ± 0.26	38.9 ± 0.6	−6.0 ± 1.2	0.00210
7[b]	268.8–319.1	42.0 ± 0.2	13.15 ± 0.08	40.9 ± 0.2	−1.7 ± 0.1	0.00195
8	207.7–258.7	41.1 ± 0.2	12.49 ± 0.10	40.1 ± 0.2	−4.3 ± 0.4	0.00119

[a] Reference 3 (solution in benzene-d_6). [b] Reference 7, gas phase.

minimize restriction of internal rotation by solvent played no facilitating role in intramolecular excimer formation.[10] These experiences contrast with the reported operation of solvent friction in rotational processes having activation enthalpies comparable to those involved in diffusion. But (see Note Added in Proof) in all such examples (see, in addition to references previously cited,[1] the works of Saltiel and co-workers[11]), experimental observations can be made at temperatures low enough to preserve significant differences in viscosity among various solvents.

An important question remains. How much slower than diffusion-controlled can reactions be and still remain sensitive to rate retardation by friction from the solvent? Further search among reactions of enthalpies of activation greater than ~5 kcal/mol should be limited to temperatures not much above ambient if large differences among viscosities are to be preserved. Among the many systems involving thermal anti–syn isomerizations that can be imagined, one has already been suggested,[1] but difficulties in synthesis may not be the only deterrent to reduction to practice: the most favorable enthalpies of activation achievable in such systems[12] may already be too high to allow detection of a significant difference between compounds of low and high extensivity.

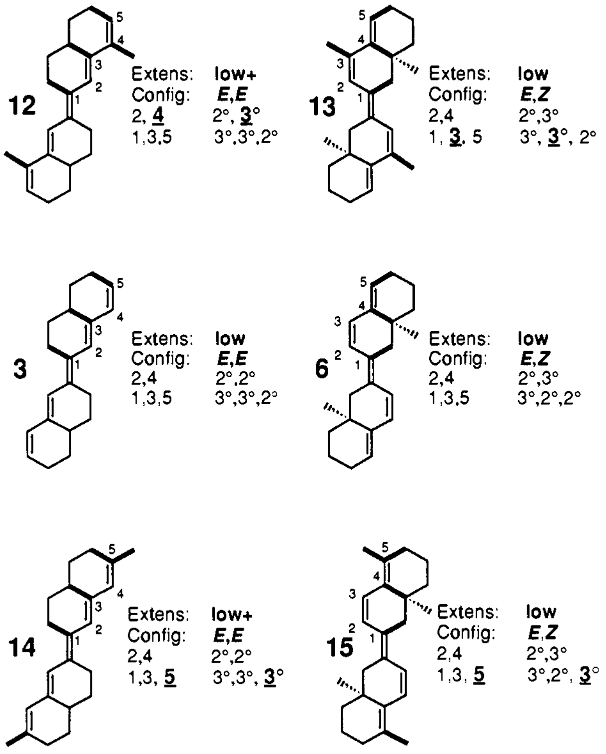
On the positive side, the difference between compounds **4** and **6** calls attention to an unanticipated effect of substitution on the stabilization enthalpy of the pentadienyl radical, further confirmation and elaboration of which are desirable for its relation to the quantum chemical theory of polyenyl radicals. However, our system offers only limited degrees of substitutional freedom. Thus, carbon atoms 4 and 5 (pentadienyl numbering) can be varied from 2° to 3° in the (*E,E*) configuration (compounds **12** and **14**, respectively) as can carbon atoms 3 and 5 in the (*E,Z*) series (compounds **13** and **15**, respectively; see Chart III).

Conclusions. Comparison of an identically configured and substituted pentaene **6** of lower extensivity with the previously reported 2,2′-bicholestadienylidene **2** of high extensivity reveals no experimentally significant difference and thus leads to withdrawal of the tentatively proffered suggestion that solvent friction might have been responsible for a 7-fold slowing in rate of thermal cis–trans isomerization. Instead it now appears that enthalpy of stabilization in the pentadienyl radical is sensitive to substitution, at least at its central carbon atom. The importance of configuration to stabilization remains unaltered.

Experimental Section

General Methods. ^{1}H NMR spectra are recorded in CDCl$_3$ or C$_6$D$_6$ solution on Bruker AM-500 (500 MHz) and AM-300 (300 MHz) instruments. ^{13}C NMR spectra are measured in C$_6$D$_6$ on Bruker AM-500 (125.8 MHz) or AM-300 (75.5 MHz) instruments. All chemical shifts are reported in ppm (δ) with respect to TMS. Infrared spectra are recorded on a Perkin-Elmer Model 337 grating spectrophotometer and reported in cm^{-1}. Liquid samples are observed as thin films on a NaCl plate or as solutions in CCl$_4$. Solid samples are measured as thin layers prepared by evaporating CHCl$_3$ solutions on a NaCl plate. UV-vis electronic spectra, measured on a Varian Cary 219 spectrophotometer, are reported as λ_{max} in nm (extinction coefficients, ϵ).

Chart III



4,4a,5,6,7,8-Hexahydro-4a-methyl-2(3*H*)-naphthalenone (9). This compound is prepared following precisely the procedure of Marshall and Fanta[4] with one small change introduced for efficiency's sake. The preparation of "*cis*-10-methyl-2-decanon-9-ol" is interrupted after "extracted with ether" and continued by drying the combined extracts over anhydrous sodium sulfate, concentrating, and distilling the residue in vacuo: bp 125–127 °C (5 Torr), 116–117 °C (1 Torr) [lit.[4] bp 82–83 °C (0.7 Torr)]; yield, 25.2 g (30%); ^{1}H NMR (CDCl$_3$) 5.70 (s, 1 H), 2.37 (m, 4 H), 1.79 (m, 6 H), 1.36 (m, 2 H), 1.22 (s, 3 H); IR 1670, 1620.

4,4′,4a,4a′,5,5′,6,6′,7,7′,8,8′-Dodecahydro-4a,4a′-dimethyl-2,2′-bi-3*H*-naphthylidene (8). A solution of 1.27 g (7.70 mmol) of the ketone **9** above in anhydrous THF is added to "titanium reagent" [from 17.3 g (91.2 mmol) of TiCl$_4$, 14 g (214 mmol) of activated zinc dust, and 10.0 mL of pyridine in 150 mL of dry THF] and processed in the usual manner.[3] The crude product is dissolved in 10 mL of dichloromethane and mixed with 4 g of silica gel. After evaporation of the solvent, the mixture is flash chromatographed (silica gel, 4.5 × 15 cm) using hexane as the eluent to give a colorless, crystalline mixture (0.45 g, R_f = 0.48) of the four stereoisomers of the triene: β-syn, (20%), α-syn (15%), β-anti (42%), and α-anti (23%). Chemical shifts in the NMR spectrum of vinyl H1 are 6.63, 6.59, 6.39, and 6.34, respectively. Three recrystallizations from anhydrous THF at −10 °C afford β-anti as colorless crystals: mp 188.5–189.5 °C; ^{1}H NMR (C$_6$D$_6$, 500 MHz; assignments based on decoupling experiments; number of H reported for only half the compound) 6.39 (s, 1 H, H1), 2.76 (m, 1 H, eq-H3, $J_{eq\text{-}e,ax\text{-}}3$ = 15.0 Hz), 2.29 (m, 2 H, ax-H3, eq-H3), 2.13 (m, 1 H, ax-H8, $J_{ax\text{-}8,eq\text{-}8}$ = 15.0 Hz, $J_{ax\text{-}8,eq\text{-}7}$ = 3.3 Hz), 1.70 (m, 1 H, eq-H$_7$, J = 12.5 Hz), 1.54–1.44 (m,

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(10) Liao, T.-p.; Morawetz, H. *Macromolecules* **1980**, *13*, 1228–1233.

(11) (a) Saltiel, J.; Sun, Y.-p. *J. Phys. Chem.* **1989**, *93*, 6246–6250. (b) Saltiel, J.; Sun, Y.-p.; Saltiel, J.; Park, N. S.; Hoburg, E. A.; Waldeck, D. H. *J. Phys. Chem.* **1991**, *95*, 10336–10342.

(12) Doering, W. v. E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6037–6043.

5 H), 1.37–1.15 (m, 2 H), 1.06 (s, 3 H); ^{13}C NMR 145.60, 127.63, 120.78, 42.18, 39.91, 35.47, 33.53, 28.68, 23.42, 22.80, 22.41; UV–vis (hexane) 286 (sh, 3.80 × 10^4), 296 (4.84 × 10^4), 307 (sh, 3.80 × 10^4); IR, 2910, 2850, 1430, 868.

The mother liquors, after most of the β-anti isomer has been removed by crystallization, consist of β-syn and β-anti (3.19:1.00) and α-syn and α-anti (1.02:1.53). After being passed through a silica gel column (hexane), concentrated, and stored in the refrigerator under nitrogen, this slightly yellow sample is used in the kinetic experiments.

4,4a,5,6-Tetrahydro-4a-methyl-2(3*H*)-naphthalenone (10). Following the procedure of Banerjee and Angadi[5] at twice the scale affords 3.06 g (31%) of **10**: bp 96–98 °C (0.75 Torr) [lit.[5] bp 110 °C (1 Torr)]; ^{1}H NMR (CDCl$_3$) 6.20 (m, 1 H), 6.12 (dd, 1 H, J_1 = 9.93 Hz, J_2 = 2.37 Hz), 5.65 (s, 1 H), 2.59 (m, 1 H), 2.44–2.27 (m, 3 H), 1.79 (m, 2 H), 1.55 (m, 2 H), 1.15 (s, 3 H).

4,4′,4a,4a′,5,5′,6,6-Octahydro-4a,4a′-dimethyl-2,2′-bi-3*H*-naphthylidene (5). To a flask containing 150 mL of anhydrous THF cooled to −10 °C are added successively 5 mL (8.7 g, 0.046 mol) of TiCl$_4$ and 4.8 g (0.074 mol) of zinc dust activated with 2% HCl. After the solution has been stirred at room temperature for 30 min, 5 mL of pyridine is added and the mixture is refluxed for 1 h. To the solution cooled to 0 °C is added 3.08 g (0.019 mol) of **10** slowly by syringe. The solution is then stirred at room temperature for 1 h and concentrated to a residue, which is dissolved in 120 mL of methylene chloride–hexane (1:3) and filtered. The filtrate is passed through silica gel and eluted with the same solvent. Removal of solvent affords 2.22 g of a viscous oil containing only small amounts of syn isomer. This product is twice crystallized from THF at 4 °C to give fine orange crystals of a mixture of α- and β-anti isomers: mp 162.9–164.2 °C; ^{1}H NMR (C$_6$D$_6$) 6.48 (s, 2 H, β-H1), 6.47 (s, 2 H, α-H1), 6.28 (dd, 4 H, J_1 = 9.63 Hz, α- and β-H8), 5.77 (m, 4 H, α- and β-H7), 2.77 (m, 4 H), 2.47 (m, 4 H), 2.27 (m, 4 H), 2.05 (m, 4 H), 1.54–1.39 (m, 16 H), 1.07 (s, 6 H, β-CH$_3$), 1.06 (s, 6 H, α-CH$_3$). This sample is stored at −85 °C under argon prior to use in kinetic studies.

6,7,8,8a-Tetrahydro-8a-methyl-2(1*H*)-naphthalenone (11). This ketone is prepared following closely the directions of Sims.[6] For purposes of identification, NMR spectra of the successive intermediates are recorded. 1,2,3,4-Tetrahydro-2-naphthol: ^{1}H NMR (CDCl$_3$) 7.11 (m, 4 H), 4.17 (m, 1 H), 3.10 (m, 1 H), 2.96 (m, 1 H), 2.86 (m, 1 H), 2.77 (m, 1 H), 2.06 (m, 1 H), 1.83 (m, 1 H); IR 3350, 3020, 2930, 1610, 1590, 1040, 745. 1,2,3,4,5,8-Hexahydro-2-naphthol: ^{1}H NMR (CDCl$_3$) 5.70 (s, 2 H), 3.99 (m, 1 H), 2.54 (s, 4 H), 2.19 (m, 1 H), 2.00 (m, 2 H), 1.89 (m, 2 H), 1.67 (m, 1 H); IR 3350, 3020, 2930, 1040. *cis*-Tricyclo[4.4.1.0^{1,6}]undec-8-en-3-ol: ^{1}H NMR (CDCl$_3$) showed cyclopropane methylene at 0.67 (d, 1 H), 0.38 (d, 1 H). Tricyclo[4.4.1.0^{1,6}]undec-8-en-3-one: ^{1}H NMR (CDCl$_3$) 5.54 (m, 2 H), 2.33 (m, 4 H), 2.19–1.99 (m, 6 H), 0.71 (d, 1 H, J = 5.3 Hz), 0.48 (d, 1 H, J = 5.3 Hz); IR 3040, 2900, 1710.

To 80 mL of a 1:3 mixture of concentrated HCl–acetic acid is added 4.98 g (0.03 mol) of this ketone. The solution is refluxed under argon for 3 h, cooled to room temperature, poured into 500 mL of water, and extracted three times with ether. The ether extracts are washed with water, saturated NaHCO$_3$, and water and then dried over MgSO$_4$. Concentration affords 4.87 g of an oil, shown by ^{1}H NMR to consist of ketones **11** and **10** in a ratio of 2:1. Chromatography on silica gel with hexane–ethyl acetate (4:1) as developing solvent yields 2.23 g (44%) of **11** as a light orange oil (R_f = 0.43): ^{1}H NMR (CDCl$_3$) 6.86 (d, 1 H, J = 9.75 Hz), 6.01 (m, 1 H), 5.08 (d, 1 H, J = 9.75 Hz), 2.30 (m, 2 H), 2.23 (m, 2 H), 1.72–1.50 (m, 2 H), 1.10 (s, 3 H).

6,6′,7,7′,8,8′,8a,8a′-Octahydro-8a,8a′-dimethyl-2,2′-bi-1*H*-naphthylidene (6). To 2.38 g (0.015 mol) of ketone **11** in 150 mL of THF are added 7.13 g (0.038 mol) of TiCl$_4$, 4.0 g (0.11 mol) of Zn, and 4.1 mL of pyridine, and the reaction is run as before. Column chromatography affords 0.84 g of an oily mixture of anti and syn isomers, which is purified by fractional crystallization (three layers) from methylene chloride at 4 °C. The leading fraction is pure *anti*-**6** as pale yellow, plate-like crystals, mp 177.2–178.2 °C, of an inseparable mixture of α- and β-isomers: ^{1}H NMR (C$_6$D$_6$) 6.54 (d, 2 H, J = 9.77 Hz, H3), 6.08 (d, 2 H, J = 9.77 Hz, H4), 5.50 (m, 2 H, H5), 2.68 (d, 2 H, J = 14.0 Hz, H1), 2.04 (m, 6 H), 1.70 (m, 2 H), 1.53 (m, 2 H), 1.45 (m, 2 H), 1.35 (m, 2 H), 1.06 (s, 6 H, CH$_3$); IR 2940, 1650, 1455, 1430, 1346.

Kinetics of Anti–Syn Isomerization of 8, 5, and 6. These studies are pursued in the manner described previously.[3] A solution of the polyene as mixtures of the α- and β-anti isomers in C$_6$D$_6$ (0.6–0.8% w/v), containing 18-crown-6 ((6-8) × 10^{-3}% w/v), is placed in an NMR tube, which has been treated previously with 1,1,1,3,3,3-hexamethyldisilazane, washed with ammonium hydroxide and acetone, and oven-dried. The samples are degassed by three vacuum freeze–thaw cycles, sealed under vacuum (10^{-3} mmHg), and protected from light while being heated in the vapors of boiling liquids.

The liquids employed are chlorobenzene (132 °C), anisole (154 °C), mesitylene (165 °C), diethyl oxalate (185 °C), undecane (196 °C), and tetralin (208 °C). The temperature of the heating bath is measured by a digital thermometer (Digisense Model No. 8528-30, Cole Parmer Instrument Company) employing a J-type thermocouple as temperature sensor (error ±0.2 °C). Temperature is recorded immediately before and immediately after each heating period. However, for longer runs, temperature is recorded every 12–18 h without disturbing the kinetic experiment. The temperature of the vapor bath has been observed to fluctuate within tolerable limits (±0.3 °C), depending upon barometric pressure and humidity. The temperature of each heating period is taken as the mean of the temperatures recorded before and after the kinetic run. The mean of the temperatures of the individual intervals gives the average temperature of the kinetic experiment.

Quantitative ^{1}H NMR spectra are measured allowing an interpulse time delay (relaxation delay and saturation period) of at least five times the longest spin lattice relaxation time (T_1) of the concerned protons. Spin lattice relaxation times (T_1's) are measured by the inversion recovery method using degassed, vacuum-sealed solutions of the substance in C$_6$D$_6$. NMR analysis is effected on a Bruker AM-500 (500 MHz) NMR spectrometer by means of the H1 signals at 6.4–6.8 (*anti*- and *syn*-**5**) and 6.5–6.7 (*anti*- and *syn*-**6**), respectively. As the α and β stereoisomers of the syn and anti isomers overlap slightly, no attempt has been made to integrate the signals separately. At the beginning and end of the reaction, the singlet of the crown ether (T_1 = 1.8 s) is also integrated as a basis for calculating total recovery. Spectra are recorded with pulse intervals of 6.85 s. Generally, accumulation of 1600–2000 scans (accumulation time: ca. 2 h) is required to achieve reasonable signal-to-noise ratios. The kinetic data are given in Tables S1 (**8**), S2 (**5**), and S3 (**6**) of the supplementary material. Reaction rates and equilibrium constants at each of the individual temperatures are optimized simultaneously by the nonlinear least-squares method to fit the reversible first-order kinetic equation to the observed data.[3] Activation parameters are calculated from the observed rate and equilibrium constants at the different experimental temperatures and are displayed in Tables I (**8**), II (**5**), and III (**6**).

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Note Added in Proof: In a quite recent publication,[13] comparisons among solvents of varying viscosities, previously believed to isolate solvent friction as a factor in processes of low barriers, are again questioned by Troe et al., who advocate pressure-induced changes in viscosity within a single solvent as a means of separating the influence of the solvent viscosity on rate from an influence on the potential energy surface.

Supplementary Material Available: Tables of unprocessed data from the study of the kinetics of thermal rearrangement of compounds **8**, **5**, and **6** (Tables S1, S2, and S3, respectively) (3 pages). Ordering information is given on any current masthead page.

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(13) Nikowa, L.; Schwarzer, D.; Troe, J.; Schroeder, J. *J. Chem. Phys.* **1992**, *97*, 4827–4835.