Beyond Butadiene II: Thermal Isomerization of the [2 + 2] Photodimer of an *all-trans*-Tetraene, (*R*)-4,4aβ,5,6,10,10a-Hexahydro-10aβ-methyl-2(3*H*)-methyleneanthracene, to a 16-Membered [8 + 8] Cycle

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Abstract: Enthalpies of stabilization of polyenyl radicals of increasing order previously obtained by thermal geometrical isomerization are applied to the ethylene−cyclobutane paradigm. Progressively lower enthalpies of activation for thermal cyclodimerization and its reverse, cycloreversion, are predicted and realized. Photochemical dimerization at −75 °C of the optically pure tetraene of the title (**1**) at the semicyclic double bond produces in the main only one (**4-*axx***) of the three allowed cyclobutanes (**4**), to which the tentative configuration *anti-exo,exo* is assigned. Equilibration among the three cyclobutanes (**4**), a slower rearrangement to a thermodynamically considerably more stable, [8 + 8] cyclohexadecahexaene (**16**), and a surprisingly slow fragmentation to **1** are studied kinetically between −42.3 and −8.2 °C. Cycloreversion of the dimer **16** to monomer **1** occurs in the range 60.4−86.6 °C ($\Delta H^{\ddagger} = 31.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = +10.8$ cal mol^{-1} K^{-1}). The ratio of the rates of stereomutation and cycloreversion is significantly larger in these 1,2-dihexatrienylcyclobutanes than in two less strongly stabilized, previously published examples. The possible extension of Doubleday's calculational finding of *entropic* control of products from cyclobutane is considered.

Introduction

Enthalpies of stabilization of polyenyl radicals obtained in one system[1−3] and incorporated into a simple paradigm lead to the prediction of some remarkably low *enthalpies* of activation for apposite, thermally induced transformations.[4] The paradigm for the present set of perturbations by polyenes (Scheme 1) is the two-step, thermal interconversion of cyclobutane and two molecules of ethylene[5] (cyclodimerization to cyclobutane in the forward direction,[6] and cycloreversion or fragmentation to two molecules of ethylene in the reverse).[7] Of the factors $\Delta\Delta_f H$ and $T\Delta\Delta_f S$ which control the position of equilibrium, enthalpy strongly favors cyclobutane by ~18 kcal mol^{-1},[8] whereas entropy, unfavorable for dimerizations in general, strongly favors ethylene at temperatures required for convenient rates of reaction.

Perturbation of the paradigm by one double bond generates butadiene and dimers *cis-* and *trans*-1,2-divinylcyclobutane. The enthalpy of activation for cycloreversion of these cyclobutanes has been predicted to be 33.8 kcal mol^{-1}.[4] This value agrees well with experimental values of 34.0 and 35.7 kcal mol^{-1}.[9] In the sterically more complex system 3-methylenecyclohexene/ *anti-* and *syn*-dispiro[5.0.5.2]tetradeca-1,8-diene (**2**; Scheme 1), experimental enthalpies of activation are 31.7 kcal mol^{-1} for cycloreversion and 30.0 kcal mol^{-1} for stereomutation.[10] The decrement of 2−4 kcal mol^{-1} is reasonably ascribed to a steric acceleration.

Perturbation by two double bonds (butadiene) leads to a polyene of the third order, hexatriene, and dimers *cis-* and *trans*-1,2-dibutadienylcyclobutane. The prediction of a further lowering of the enthalpy of activation for cycloreversion to 27.0 kcal mol^{-1} compares to an experimental value for **3** of 24.3 kcal mol^{-1}. Here too, the actual value is again lower than the predicted one by ~3 kcal mol^{-1}.

Results: The 16-Membered Ring

In the present work, perturbation of the paradigm is extended to a polyene of the fourth order (Scheme 1). An enthalpy of activation of $\Delta H^{\ddagger} = 22.4$ kcal mol^{-1} is estimated for fragmentation of the hypothetical, unsubstituted 1,2-dihexatrienylcyclobutane to a pair of octatetraene molecules.[11] In the rigid example examined here (**4** of Scheme 1), the steric factor may be expected to lower the value to ~19 kcal mol^{-1} in analogy to the two examples noted above.

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[11] The procedure is depicted explicitly in Scheme 2 of ref 4.

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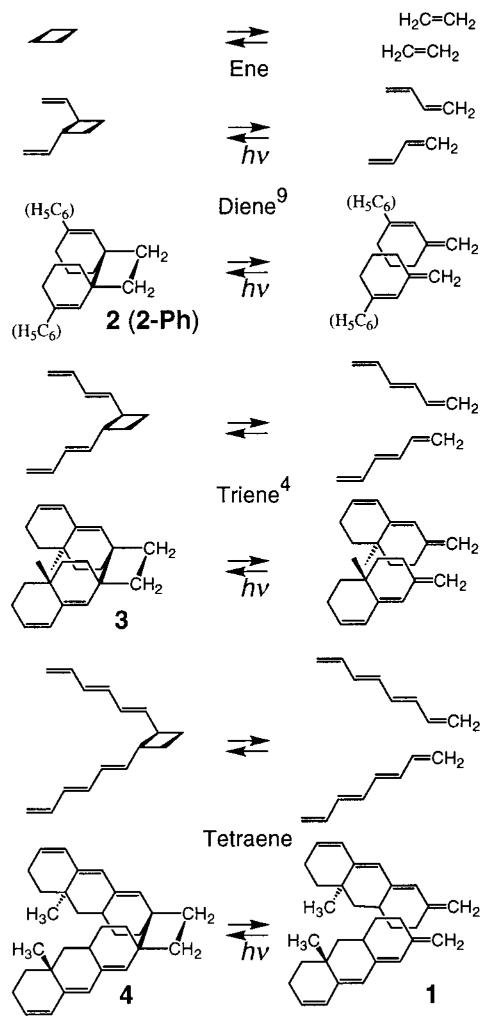
Scheme 1



Tetraene **1′** (demethyl-**1**; throughout, the prime will denote compounds without the methyl groups) was the initial subject of our study. It had already been prepared as a relatively unstable, colorless, crystalline compound of mp 110 °C from an available ketone, **7′**[1] (demethyl-**7**), by application of a conventional Wittig reaction.[12] Although its structure followed quite reasonably from the method of preparation, additional support came from its mass, UV, and ^{13}C NMR (normal abundance) spectra, in which three quaternary olefinic carbon atoms were recognized by the DEPT technique (Figure 1).

More rigorous confirmation of structure is obtained from a sample of **1′** enriched with ^{13}C (99.4%) in the *exo*-methylene position. This tetraene, **1′**-^{13}***C***, shows in its ^{1}H NMR spectrum a typical ^{13}C−^{1}H coupling constant of 156 Hz,[13] and a strong resonance at 110.5 ppm for the *exo*-methylene group in its ^{13}C NMR spectrum, which is otherwise identical to that of the unlabeled sample. Two quaternary carbon atoms, at 144.6 ppm (C-2) and 141.3 ppm (C-9a), are coupled to the *exo*-methylene-^{13}*C* carbon atom by 72 and 7.9 Hz, respectively, presumably as a consequence of one-bond and three-bond, carbon−carbon couplings, respectively, two-bond coupling usually being small.

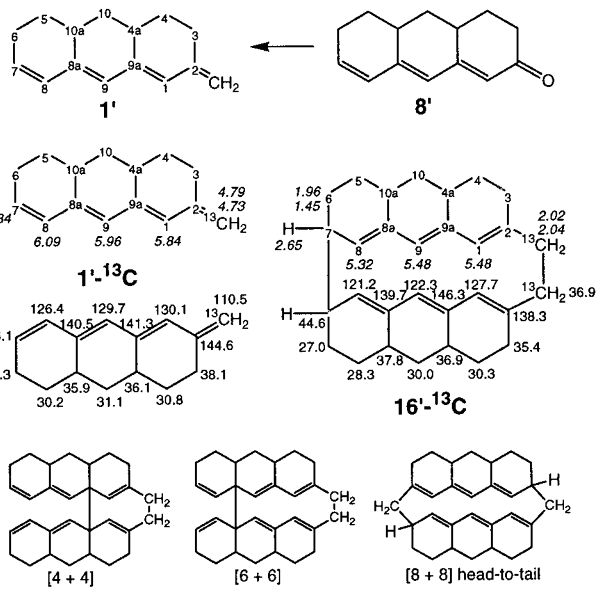


Figure 1. NMR chemical shifts (δ scale, 500 MHz) assigned to hydrogen atoms (ppm, italics) and to carbon atoms for **1′**-^{13}***C*** and **16′**-^{13}***C***, along with diagrams of [4 + 4] and [6 + 6] head-to head dimers of **1′**, and the [8 + 8] head-to-tail dimer **16′**.

On irradiation at 0 °C in toluene-d_8 with a medium-pressure, mercury lamp and benzophenone as sensitizer, unlabeled tetraene **1′** does not yield a cyclobutane, but compound **16′** as a yellow precipitate. Its ultraviolet absorption spectrum (λ_{max} 278 nm, log ϵ 4.40) is consistent with that of a conjugated triene,[14] while its mass spectrum (*m*/*e* 396) points to a dimer. In its ^{13}C NMR spectrum, 15, not 30, identifiable absorptions indicate a structure of 2-fold symmetry, while two pairs of three peaks (146.3, 139.7, and 138.3 ppm) can be identified as quaternary olefinic carbon atoms by application of the DEPT method. A dimer of the [8 + 8] type, but not of the [6 + 6], [4 + 4], or [2 + 2] type, satisfies these observations. In its ^{1}H NMR spectrum, the most important feature is a hydrogen atom at 2.65 ppm identified as allylic H-7 by homonuclear decoupling of olefinic H-8 at 5.32 ppm, and by the effect of homonuclear decoupling of H-7 on two aliphatic H atoms at 1.45 and 1.99 ppm (see Figure 1).

Although these observations are consistent with a 16-membered cyclic structure, they do not suffice to distinguish between head-to-head and head-to-tail alternatives. Crystallographic analysis might have resolved the issue, but we have been unable to obtain a suitable single crystal. Examination of **16′**-^{13}***C***, prepared from **1′**-^{13}***C*** labeled in the exocyclic methylene group, has, however, allowed the distinction to be made. All the peaks in the spectrum of unlabeled **16′** can be seen again in the spectrum of **16′**-^{13}***C***, except for the peak at 36.88 ppm, which is overwhelmed by the much stronger peak at 36.91 ppm. The resonance of the quaternary carbon atom at 138.3 ppm is split into a doublet (J = 40 Hz) by one-bond, carbon−carbon coupling. There are some small peaks around these peaks which might be due to weak two-bond, carbon−carbon coupling. Observation of only a *single* coupling between the ^{13}C-labeled methylene and an adjacent quaternary carbon is strongly supportive of a head-to-head structure for the dimer. A head-to-tail structure would have been expected to show coupling with *two* adjacent carbon atoms. In the ^{1}H NMR spectrum of **16′**-^{13}***C***, the expected large (120 Hz) coupling between ^{13}C and its two protons (2.02 and 2.04 ppm) remains *unchanged* on homonuclear decoupling by irradiation of the proton at C-7 (2.65 ppm). This observation is consistent with the methylene-^{13}*C*

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(12) We are indebted to Dr. Keshab Sarma for the procedure for this preparation.

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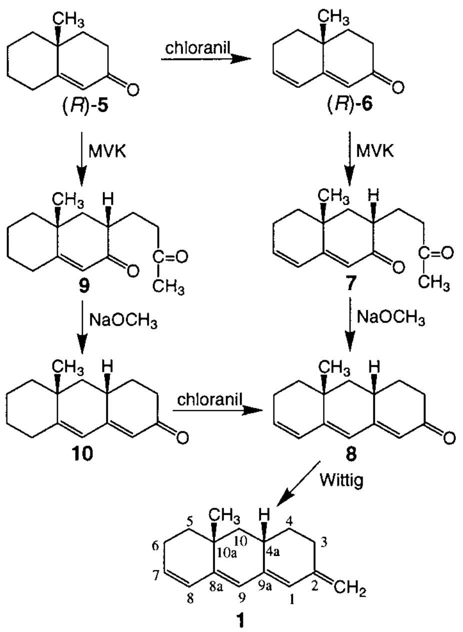
Scheme 2



groups not being attached to C-7, and is fully consistent with the head-to-head structure (see Figure 1 for numbering and collection of resonances).

In the ^{13}C NMR spectrum of unpurified **16′-^{13}*C***, four peaks, at 36.82, 36.58, 36.14, and 35.90 ppm, of lower intensity correspond to two methylene-^{13}*C* carbon atoms, appearing as two doublets at 36.70 and 36.02 ppm, each having a coupling constant of 30 Hz. These peaks are probably associated with contamination by minor dimers of unsymmetrical structure, that is, having 30 spectroscopically distinguishable types of carbon atoms. Although cycloreversion of **16′** to **1′** occurs at temperatures above 60 °C, preliminary kinetic studies revealed substantial deviation from first-order behavior. Contamination by one or more minor isomers differing in the rates of fragmentation by a factor of ~2 seemed to be the cause.

In the hope of circumventing this obstacle to generating reliable activation parameters, attention was directed to optically pure **1**, the 10a-methyl analogue of **1′**. By this device, which had been used successfully in earlier work, the number of possible, stereoisomeric products of photodimerization is reduced from the six for racemic material to three.[4]

Preparation of optically active **1** was accomplished by two closely related routes (Scheme 2). Both started from the Revial–Pfau compound (***R***)-**5**, readily available in optically pure form.[4] One way around [(***R***)-**5**, **-9**, and **-10**] gives **1** in relatively low yield, while the other [(***R***)-**6**, **-7**, and **-8**] gives a good yield. Irradiation at 0 °C of the monomeric tetraene **1** generates a single compound, **16**, the physical properties of which are so similar to those of **16′** that a 16-membered structure can be confidently assumed.

Thermal decomposition of **16** to **1** follows a now strictly first-order rate law. The kinetics has been studied without complication in the range 60–87 °C. Specific rate constants and activation parameters are given in Table 1. The positive entropy of activation, $\Delta S^{\ddagger} = 11.7$ eu, accords with a loosening of the system as breaking a single bond generates a diradical intermediate in the cycloreversion.

The Four-Membered Ring Compounds

Irradiation of the monomeric, optically pure tetraene **1** at −75 °C in toluene-d_8 reveals a richer story. The major, perhaps exclusive, product is a thermally unstable compound, **4a**, which rearranges slowly to **4b** and, more slowly, to **4c** even while its NMR spectrum is being observed at −40 °C. Over time—the more rapidly, the higher the temperature—all three stereoisomers of **4** are replaced by the macrocycle **16** and, to a much smaller extent, monomer **1**.

Lacking appropriate experimental facilities, we have not been able to separate, alone isolate, the three unstable components of **4**. Their presence (and relative concentrations) are inferred by ^{1}H NMR spectroscopy, while their structures as the three possible cyclobutanes resulting from dimerization at the exocyclic double bond are assigned by analogy with the photochemistry of the two lower relatives of **1** of orders 2 and 3 (see Scheme 1).[4,10] An exciplex constructed from two parallel monomers overlapping so as to minimize steric repulsion between methyl groups might be expected to favor an *anti-exo,exo* configuration, and lead predominantly to cyclobutane **4a** (**4-*axx*** in Figure 2).

In the plot of concentration against time in Figure 3 (−29.4 °C), stereomutation of **4a** to **4b** is seen to be initially the fastest reaction among the three cyclobutanes. As this interconversion approaches equilibrium, **4b** passes through a maximum as it contributes increasingly to the slower generation of **4c** and **16** (and to a much lesser extent **1**). Thereafter, as pictured in a similar diagram at −8.2 °C, the three cyclobutanes **4** appear to reach a steady state in which all three contribute to the rearrangement to **16**. In this pseudoequilibrium, the concentrations of **4a** and **4c** are essentially equal, while that of **4b** is favored by a factor of ~2, incidentally the same as the statistical factor. Note that the two methyl groups in all configurations of **4** are far apart (see the 3D representation of **4c** (**4-*ann***) in Figure 2) and that this qualitative impression is confirmed by the essentially identical steric energies calculated for the three stereoisomers by molecular mechanics (Figure 4).

The prospect of extracting the 12 specific rate constants implied in Figure 2, and of obtaining their temperature dependences with acceptable accuracy given only one of the components of **4** as starting material, though possible in theory, cannot be realized in practice. Nonetheless, the kinetics of the system has been studied, encouraged in part by a question recently brought into focus by the work of Doubleday (vide infra).

The kinetics of the system **4**, **16**, and **1** was examined extensively over a range of temperature from −42.3 to −8.2 °C in 17 independent runs. Several not fully resolved difficulties were encountered, including the poorly defined time taken for a sample of **1**, freshly irradiated at −75 °C, to reach thermal equilibrium in the NMR spectrometer used for analysis, inaccuracies in the measurement of temperature in the NMR tube, and fluctuations in reaction temperature over time. The set of data relating relative concentrations and time (Table SI-1 of the Supporting Information) is given in part to satisfy the intrepid reader who may wish to explore alternate approaches to handling the data for this seriously underdetermined system.[15]

Treatment of the sum of the rearrangements of **4a**, **4b**, and **4c** (∑**4**) to **16** as a first-order transformation leads to the specific rate constants in Table 2, while a temperature dependence of acceptable precision is given in Table 3. The simplification of combining all stereoisomers of **4** into a single entity is easier to accept at the higher temperatures than at the lower ones. At the higher temperatures, a steady state among ∑**4** appears to

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[15] Attempts to use a more realistic kinetic model including up to seven differential equations were unproductive. The program did not lead to convergence, and seemed to require negative rate constants in its efforts to minimize the sum of differences.

Table 1. Specific Rate Constants and Activation Parameters for the Cycloreversion of the [8 + 8] Dimer **16** to Two Molecules of **1** in Benzene-d_6

T, °C	$k_1{}^{a,b}$	T, °C	$k_1{}^{a,b}$	T, °C	$k_1{}^{a,b}$
60.4 ± 0.9	0.290 ± 0.012	68.8 ± 0.3	0.993 ± 0.022	86.6 ± 0.1	10.26 ± 0.29
60.4 ± 0.9	0.296 ± 0.017	68.8 ± 0.3	0.994 ± 0.040	86.6 ± 0.1	10.66 ± 0.58

Arrhenius Parameters[b]: $E_a = 32.51 \pm 0.44$ kcal mol^{-1}, log $A = 15.77 \pm 0.28$

Eyring Parameters[b,c]: $\Delta H = 31.8 \pm 0.4$ kcal mol^{-1}, $\Delta S = +11.7 \pm 1.3$ cal mol^{-1} K^{-1}

[a] k in units of 10^{-5} s^{-1}. [b] Standard deviations are at the 95% confidence level. [c] Calculated at 346.7 K.

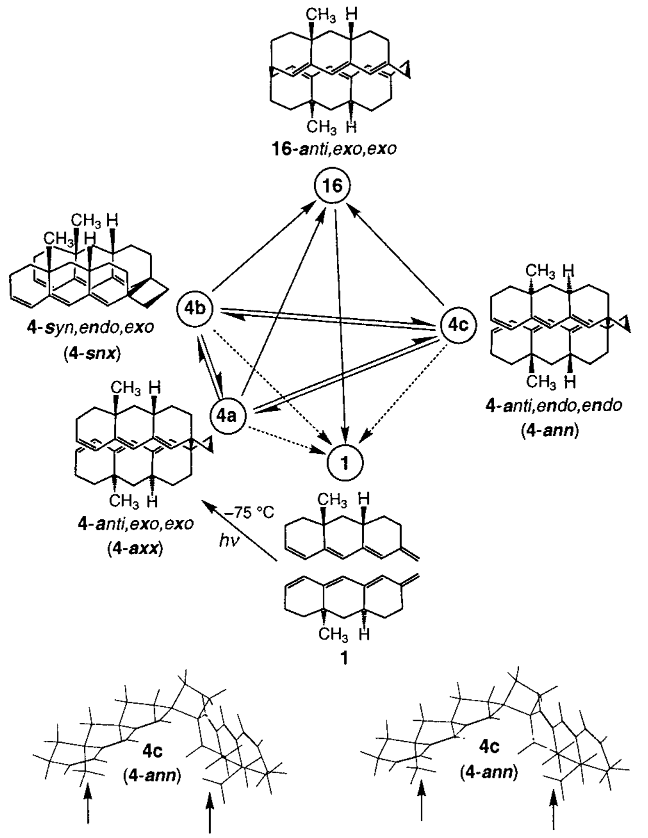


Figure 2. Kinetic scheme for the six interconversions relating **4a**, **4b**, and **4c**, their three ring enlargements to **16**, and their three fragmentations each to two molecules of **1**. A 3-D representation of **4c** (**4-*ann***), the stereoisomer expected to show the greatest steric repulsion between methyl groups, is shown at the bottom.

have been reached, but not at the lower temperatures (see Figure 3). The accuracy of the results is doubtless lower than the precision.

Data relating to the interconversion of **4a** and **4b** are handled as a system of reversible first-order reactions. Reasonable rate constants are obtained if only the early points are used where a linear approximation can be visually entertained (see the plot of data at −29.4 °C in Figure 3). This model is an oversimplification owing to several factors: both **4a** and **4b** are rearranging simultaneously to **16**, **4c**, and **1** in that order, but not necessarily at equal rates, the model is applicable only over a limited range of temperature, and a value for the unknown equilibrium constant must be assumed. The statistical factor for **4b** leads us arbitrarily to take $K = 2$.

The generation of **4c** is sensibly slower, and is likewise handled by using only early points where approximation of a first-order interconversion of (**4a** + **4b**) and **4c** can be entertained. A value of $K = 1/3$ is assumed in the calculations.

Fragmentation to **1** is so much slower that its relative concentrations are small and subject to large analytical errors. The resulting low degree of precision is reflected in high uncertainties in the rate constants and derived activation parameters. Recall that **1** can also be formed from **16** at higher temperatures (Table 1). This mode has a calculated specific rate constant at −8.2 °C of ~1 × 10^{-11} s^{-1}, and therefore makes a negligible contribution to the formation of **1** at the lower temperatures.

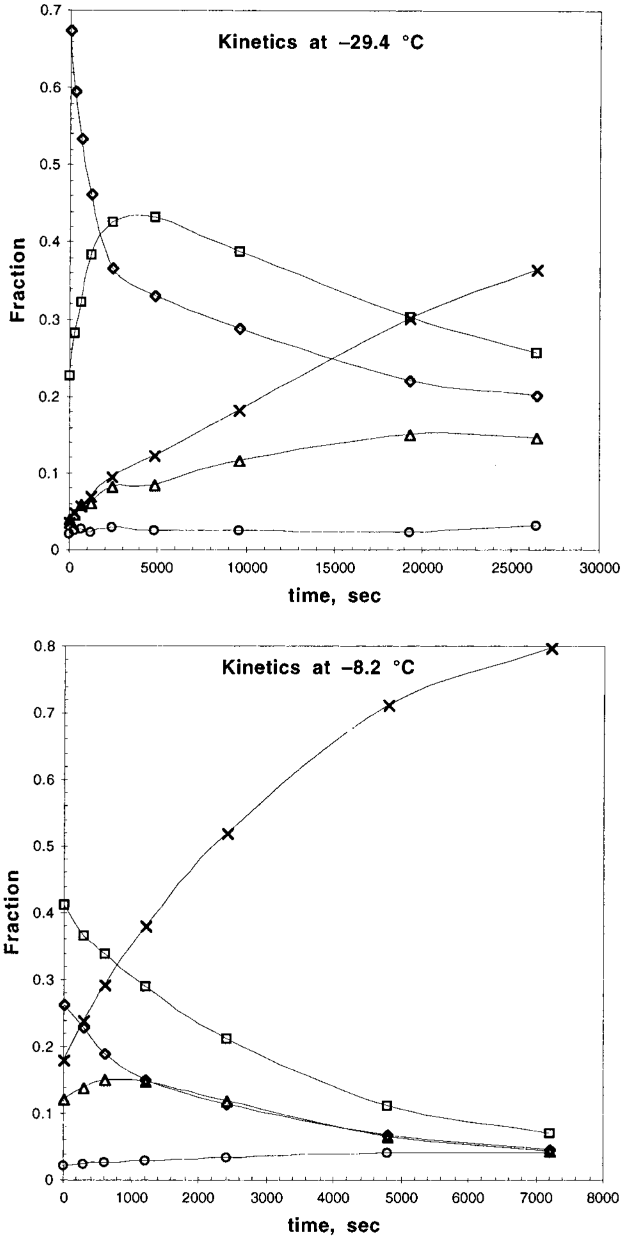
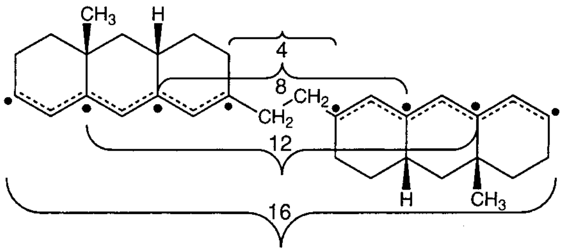


Figure 3. Fractions of **4a** (diamonds), **4b** (squares), **4c** (triangles), **16** (times signs), and **1** (circles) (ordinate) against reaction time in seconds (abscissa) at two temperatures.

All worthy rate constants are collected in Table 2, while derived activation parameters are collected in Table 3, and depicted graphically in Figure 5.



Ring Size		*anti exo,exo*	*syn exo,endo*	*anti endo,endo*
Cyclobutane (**4**)	[2 + 2]	⇗**50.5**	⇗ **51.9**	⇗**49.8**
Cycloöctadiene	[4 + 4]	76.5	97.3	75.6
Cyclododecatetraene	[6 + 6]	76.2	106.6	89.5
Cyclohexadecahexaene (**16**)	[8 + 8]	⇗**35.7**	61.7	61.1

Figure 4. Steric energies calculated by MM2 for four ring sizes of the symmetrical, head-to-head, C_{30} dimers of tetraene **1** [(*R,R*) configuration, kcal mol^{-1}].

Table 2. Specific Rate Constants (s^{-1}) from Kinetic Studies of the System **1**, **4**, and **16** in Toluene-d_8 (Figure 2)

T, °C	1/*T*, K	**4a** ↔ **4b**[a,b]	(**4a** + **4b**) ↔ **4c**[a,c]	(**4a** + **4b** + **4c**) → **16**	(**4a** + **4b** + **4c**) → **1**
−42.3	0.004332	4.333E−5	6.949E−6	2.122E−6	
−42.3	0.004332	4.675E−5	8.919E−6	1.220E−6	
−35.3	0.004204	1.895E−4	2.735E−5	7.092E−6	
−35.3	0.004204	1.749E−4	2.630E−5	6.990E−6	
−35.3	0.004204	2.047E−4	2.487E−5	6.462E−6	
−29.4	0.004103	6.059E−4	1.194E−4	1.602E−5	
−27.2	0.004066	5.931E−4	9.228E−5	1.877E−5	
−27.2	0.004066	5.701E−4	1.242E−4	2.119E−5	
−25.1	0.004031	1.009E−3	1.747E−4	2.267E−5	
−24.9	0.004028	1.074E−3	1.854E−4	3.472E−5	
−22.1	0.003983		2.657E−4	3.955E−5	3.724E−7
−22.1	0.003983		3.587E−4	4.294E−5	6.068E−7
−16.3	0.003893		5.420E−4	7.210E−5	8.037E−7
−11.7	0.003825		5.485E−4	1.023E−4	3.331E−6
−11.7	0.003825			6.648E−5	1.438E−6
−11.7	0.003825			1.396E−4	2.357E−6
−8.2	0.003774			2.097E−4	3.682E−6

[a] Rate constants calculated for the reversible, first-order model: $\ln[(KA_t + B_t)(/KA_o + B_o)] = (k_{-1} + k_1)/t$. [b] Assumed $K = 2$. [c] Assumed $K = 1/3$.

Discussion: Thermochemical Considerations

Thermochemistry in systems such as this one provide important arguments for and against hypothetical structures, and facilitate predictions of the effect of perturbations on reactions of paradigms. Heats of formation have been estimated by both the method of group equivalent values (gev)[16] and the molecular mechanical program of Allinger[17] as elaborated by W. R. Roth (MM2EVBH). The former seeks to reproduce the available thermochemical experimental data[18] as generalized partial heats of formation for simple groups, subject to several empirical corrections of necessarily limited scope. The latter has been optimized for hydrocarbons by parametrization to a body of data enlarged by the inclusion of otherwise excluded heats of hydrogenation, and by addition of the extended valence bond approach of Malrieu and Maynau.[19] Between the contents of Table 4 and Scheme SI-1, the resulting thermochemical quantities and their derivation seem transparent. It needs only to be explained that values in column 4 are the difference between values in columns 2 and 3, and reflect the superiority of MM2 EVBH for the calculation of elements of strain that elude the gev method.

MM2 calculations of steric energy (Figure 4) have already shown their usefulness in supporting the intuitive conclusion that the methyl groups in **4** are too far apart to give rise to significant thermochemical differences among the three stereoisomers. In contrast, thermochemical calculations indicate very large unfavorable interactions of the methyl groups in the two unseen configurational isomers of **16**, and afford a rationalization for the appearance of **16** in only one configuration.

The relatively much higher steric energies of the 8- and 12-membered analogues of **4** and **16** not only render their appearance highly unlikely (under thermodynamic control) but also render improbable their involvement as nonisolable intermediates in the formation of **16** from **4** in a succession of two Cope rearrangements. If the enthalpy of activation for the Cope rearrangement of *cis*-divinylcyclobutane, 23 kcal mol^{-1},[9] is taken as a lower estimate, addition of calculated incremental strain energies of more than 25 kcal mol^{-1} in the 8- and 12-ring compounds (Figure 4) places them out of reach of an intramolecular rearrangement rapid at 0 °C. The situation stands in contrast to the ring expansions so elegantly developed by Wender and co-workers.[20]

A heat of formation of the hypothetical, bisheptatrienyl intermediary diradical (Figure 4) can be estimated from the (MM2EVBH) heat of formation of **1** by a straightforward transference of the stabilization energy ascribed to the heptatrienyl radical to the dimerization of **1**. The difference between the estimated heat of formation of **16** ($\Delta_f H° = +35.8$ kcal mol^{-1}) and that of the diradical ($\Delta_f H° = +67.8$ kcal mol^{-1}) then corresponds to an estimate of the enthalpy of activation for fragmentation of 32.0 kcal mol^{-1}. Agreement with the experimental value of +31.7 kcal mol^{-1} is good. The unsatisfactory agreement obtained by employing the values for the heat of formation of **16** estimated by the gev method is owed to the inability of this method to cope with the strain energy in the 16-membered ring.

In essence, this work has added a third, successful test of the thesis that stabilization energies of polyenyl radicals evaluated in one reaction can be transferred to a substantially different system. Extension to a polyene of order 4 has led to a large acceleration qualitatively in accord with prediction. The range of temperature covering convenient rates of stereomutation has decreased from 350 to 400 °C for the paradigm, through 70−110 °C for 1,2-divinyl, to −20 to 0 °C for 1,2-dibutadienyl, and now to −40 to −20 °C for the 1,2-ditrienyl system.

Quantitative confirmation of the thesis has been less precise than would have been wished for two reasons. The first applies to the entire series. Predictions have been based on unsubstituted models, whereas in practice more highly substituted, rigidly *all-trans* examples have been studied to avoid numerous side reactions. The resulting measured enthalpies of activation have been 3−4 kcal mol^{-1} lower than predicted. These discrepancies are reasonably ascribed to a small steric acceleration, a proposition that finds support in the difference of 9.4 kcal mol^{-1} between the two heats of formation given for **4a** in column 4 of Table 4. Roughly half (twice the discrepancy of 2.6 kcal mol^{-1} for **1** in column 4) comes from an intrinsic strain in the hydroanthracene system that is conserved on ring opening. The

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Table 3. Arrhenius Parameters from the Kinetics of the System **4**, **16**, and **1**

reaction	E_a[a,b]	log *A*	$\Delta H^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [c,d]
4a → **4b**	20.0 ± 1.9	14.60 ± 1.7	19.5 ± 1.9	+6.6 ± 8.0 (−1.1)
(**4a** + **4b**) → **4c**	18.7 ± 2.3	14.14 ± 2.1	18.2 ± 2.3	−2.4 ± 9.4 (−4.9)
(**4a** + **4b** + **4c**) → **16**	15.9 ± 1.5	9.39 ± 1.3	15.4 ± 1.5	−17.2 ± 5.9 (−8.5)
(**4a** + **4b** + **4c**) → **1**	19.8 ± 8.6	10.9 ± 7.2	19.3 ± 8.6	−10.3 ± 33.2 (−17.4)
16 → **1**	32.5 ± 0.4	15.8 ± 0.3	31.8 ± 0.4	+11.7 ± 1.3

[a] In kcal mol^{-1}. [b] Standard deviations at the 95% confidence level. [c] Calculated at −25.6 °C. [d] Values in parentheses are based on the weighted mean, $\Delta H^{\ddagger} = 17.56$ kcal mol^{-1}.

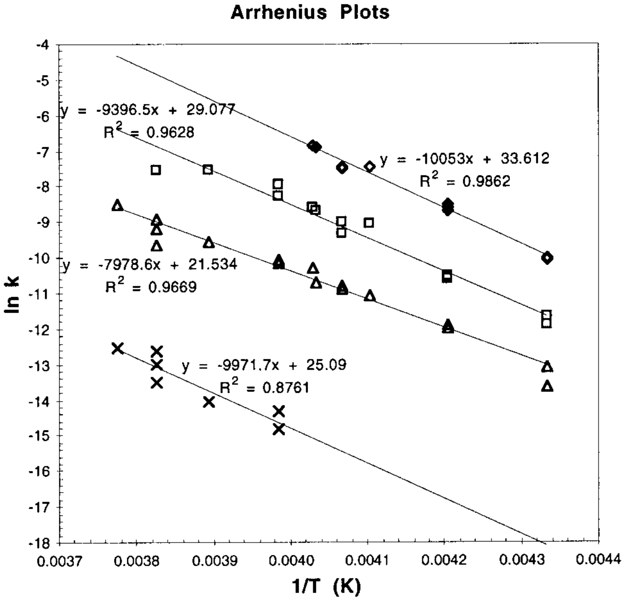

Figure 5. ln *k* (ordinate) versus 1/*T* (K) (abscissa) for the reactions of **4a** to **4b** (diamonds), (**4a** + **4b**) to **4c** (squares), (**4a** + **4b** + **4c**) to **16** (triangles), and (**4a** + **4b** + **4c**) to **1** (times signs) (see Table 3).

Table 4. Thermochemistry of **1**, **4a**, **16**, and the Diradical in Common

compound	$\Delta_f H_{(\mathrm{Roth})}$[a,b]	$\Delta_f H_{(\mathrm{Benson})}$[a,c]	$\Delta\Delta_f H_{(\mathrm{strain})}$[a,d]
1	27.6	25.0	2.6
4a	50.7	41.3[e]	9.4
16	35.8	15.1	20.7
diradical	67.8[f]	62.6[f]	5.2

[a] In kcal mol^{-1}. [b] Heats of formation calculated by the molecular mechanical program MM2EVBH. [c] Heats of formation estimated by the group equivalent values of Benson. [d] The difference between values in columns 2 and 3 is identified with the energy of strain unable to be included in the Benson value. [e] This value includes cyclobutane strain of 26.2 kcal mol^{-1}. [f] Estimated by the addition to twice the heat of formation of **1** of 43.5 kcal mol^{-1} ($2C_2H_4 \rightarrow -(CH_2)_4-$), 2*K* (conjugative interaction 3.75 kcal mol^{-1}), and 2(SE$_3$) (−19.2 kcal mol^{-1}, the stabilization energy of a heptatrienyl radical).

remainder of 4.2 kcal mol^{-1} arises from the tetrasubstituted nature of the cyclobutane ring, and is available sterically to accelerate the opening of the ring to the diradical.

The second reason applies to the current example in which experimental difficulties arising from the inconveniently low temperatures required for kinetic studies have been incompletely resolved. The four enthalpies of activation have fallen in the range of 16−20 kcal mol^{-1} in satisfactory agreement with the predicted value of 22.4 kcal mol^{-1}, when decreased as noted above by the steric correction of 3−4 kcal mol^{-1}.[4,10] The weighted mean of these activation enthalpies, 17.6 kcal mol^{-1}, agrees surprisingly well with the difference, 17.1 kcal mol^{-1}, between the estimated heat of formation of the diradical (+67.8 kcal mol^{-1}) and the heat of formation of **4a** (50.7 kcal mol^{-1}) (MM2EVBH values in Table 4, column 2).

Entropic Control of Products?

In a series of exceptionally penetrating, theoretical explorations of the role of diradical intermediates in the thermal transformations of cyclopropane and cyclobutane, Doubleday has reached a striking conclusion that choices among competing pathways out of a "common diradical intermediate" ("caldera")[21] are under the control of entropy alone.[22] In cyclobutane, more apposite to the present work, these paths or "exit channels" involve internal rotations about the C1−C2 and C2−C3 bonds followed by either reclosure or fragmentation to ethylenes.[23] His work brings a question into sharp focus: Are cyclobutanes *in general* subject to control by entropy alone, or is this attribute confined to the paradigmatic unsubstituted cyclobutane?

A theoretical answer to the question could come from calculations on 1,2-dimethylcyclobutane. For an experimentally based answer, careful studies of the temperature dependence in prudently selected systems of not obviously concerted thermal rearrangements of two, or preferably more, disparate exit channels may be helpful. In principle, the present example appears to be ideal. It has three dissimilar exit channels: stereomutation, a novel ring enlargement, and fragmentation. In practice, obtaining Arrhenius parameters for the 12 specific rate constants at a high enough accuracy to elucidate the balance between control by entropy and enthalpy is problematical, if not fantastical.

At this point, we can do little more than explore the consequences of accepting the generality of Doubleday's conclusion that all three processes would have had in common a single enthalpy of activation for entrance into the caldera, and that the weighted mean of 17.6 kcal mol^{-1} would be its value! The corresponding set of controlling entropies of activation then becomes calculable (given in Table 3, last column, in parentheses). Those relating to the interconversions among **4** are small, and consistent with those found for the two lower homologues. That for rearrangement to the conformationally more rigid **16** is—not unreasonably—more negative.

That for fragmentation to **1**, which might intuitively have been expected to be positive, is provocatively negative. The unexpectedly slow rate of cleavage of **4** to **1** appears to fall in line with a positive correlation between increasing stabilization in the diradical intermediates and ratios of stereomutation to fragmentation, k_{st}/k_{fr}. In the sequence 1,2-dideuteriocyclobutane,[24] **2**, **2(Ph)**, **3**, and **4** (Scheme 1), these ratios, although of varying accuracy and precision, are, respectively, ∼0.3 (380

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(21) A sobriquet to encompass "common diradical intermediate", "continuous diradical", and "twixtyl".

(22) (a) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; Page, M.; McIver, J. W., Jr.; Mullally, D. *J. Am. Chem. Soc.* **1984**, *106*, 447−448. (b) Doubleday, C., Jr.; Page, M.; McIver, J. W., Jr. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 331−341. (c) Doubleday, C., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 11968-11983. (d) Doubleday, C., Jr. *Chem. Phys. Lett.* **1995**, *233*, 509−513. (e) Doubleday, C., Jr. *J. Phys. Chem.* **1996**, *100*, 15083−15086.

(23) Unobserved pathways such as rearrangement to butene, or fragmentation to butadiene and dihydrogen, which we guess are under enthalpic control, are not included in the survey.

(24) Chikos, J. S. *J. Org. Chem.* **1979**, *44*, 780−784.

°C), ~0.5 (100 °C), ~6 (43.6 °C), ~25 (43.6 °C), and ~4 × 10^3 (−25.1 °C).

In terms of entropy alone as the controlling factor, we might then speculate that the number of simultaneous adjustments in bond distances required to transit from polyenic cyclobutane to polyenyl radical increases with order. A convincing answer to the question of where along the continuum from complete control by enthalpy to complete control by entropy the transformations in the present system lie will require greater accuracy than we have been able to provide.

The facile thermal rearrangement of **4** to **16** appears to be a novel ring enlargement, but is in some respects quite similar to the dimerizations developed by Glatzhofer and Longone in the paracyclophane series.[25] An important difference lies in the method of generation. In contrast to the purely aliphatic polyenes of our series, their polyenes dimerize thermally without being obliged to pass over a cyclobutane stage, presumably owing to the extra stabilization afforded to the diradical stage by the development of aromatic character.

Whether the small, extra degree of stabilization in the next homologue in our series, a pentaene, would be enough to facilitate thermal dimerization is unpredictable. That a 20-membered ring should be formed by way of the cyclobutane seems highly likely. The calculated difference in steric energy between the 20-membered and related 16-membered ring is −38 kcal mol^{-1}, more than enough to favor the former under thermochemical control, even without the extra fillip of two more units of conjugative interaction.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM-500 (^{1}H, 500 MHz; ^{13}C, 125.8 MHz) instrument in $CDCl_3$, unless otherwise noted, and are reported in parts per million from tetramethylsilane (δ) [$CDCl_3$ (7.24 ppm), benzene-d_6 (7.14 ppm)]. Differentiation among the types of carbon atoms in the ^{13}C NMR is based on the DEPT technique [*q*, quaternary; *t*, tertiary; *s*, secondary; *p*, primary].[13] Spin−lattice relaxation times (T_1) were determined by the inversion−recovery method on vacuum-sealed solutions in toluene-d_8. IR spectra, reported in cm^{-1}, were recorded on a Nicolet Impact 400D FT-IR instrument. Samples, if liquid, were measured as a thin film on a NaCl plate and, if solid, as a thin layer prepared by evaporation of a solution in $CHCl_3$ on a NaCl plate. UV−vis spectra were measured in spectrograde hexane on a Hewlett-Packard 8452A diode array spectrophotometer or a Varian Cary 1E UV−vis spectrophotometer [λ_{max}, nm (log ϵ)]. High-resolution mass spectra were measured on a JEOL AX 505 spectometer equipped with a data recovery system. Specific rotations were measured on a Perkin-Elmer Polarimeter 241; enantiomeric excess (ee) was determined with a Hewlett-Packard 5890 Series II gas chromatograph employing a Chiraldex G-TA column (20 m × 0.25 mm i.d. × 0.125 mm film, Advanced Separation Technology, Inc.). Melting points (mp's) were taken with a Thiele tube, and are not corrected. A 450 W, medium-pressure HANOVIA mercury lamp, model 679A36, or a GE 275 W sun lamp was used for photochemical reactions.

4,4a,5,6,10,10a-Hexahydro-2(3*H*)-methyleneanthracene (1′). (a) This tetraene was prepared from its precursor ketone **8′** (Scheme 1) by a Wittig reaction[2] developed by Keshab Sarma (see (b) below for details).[12] The yield depends on the time of reaction following addition of the ketone at 0 °C to the ylide solution, and the time of stirring thereafter at room temperature. Duplicate runs for 1 h at 0 °C and 2 h at room temperature afford yields of 47% and 53% of theory, respectively, while runs for 3 and 17 h at room temperature lead to lower yields of 32% and 27%, respectively. After chromatography on silica gel, colorless crystals of **1′** were obtained: mp 105−106 °C; UV−vis 294 (4.24), 306 (4.41), 322 (4.38).

1′ is unstable at room temperature, gradually being converted to a yellow polymer, which can, however, be removed by flash chromatography with hexane on silica gel, or basic alumina.

1′-^{13}*C*. (b) A 5 mL sample of a 2.5 M solution of *n*-butyllithium (*n*-BuLi) (Aldrich) in hexane was added slowly over a 5 min period to a cooled (ice−water bath) suspension of methyl-^{13}*C*-triphenylphosphonium iodide (^{13}C, 99.4%, 2.00 g, 5.00 mmol) in 15 mL of tetrahydrofuran (THF). To the resulting solution was then slowly added ketone **8′** (0.51 g, 2.5 mmol) in 3 mL of THF. After being stirred for 3 h as the temperature rose to ambient, the reaction mixture was treated with 0.5 mL of water, evaporated to dryness, and triturated with 5 mL of hexane. The hexane solution was passed through a basic alumina column (2.5 cm i.d. × 20 cm, hexane as eluent), and concentrated to yield 0.31 g (62%) of 4,4a,5,6,10,10a-hexahydro-2(3*H*)-methylene-^{13}*C*-anthracene (**1′-^{13}*C***) as colorless crystals: mp 110 °C; ^{1}H NMR 6.09 (d, 1H, J = 7.7 Hz, H-8), 5.96 (s, 1H, H-9), 5.84 (m, 2H, H-7 and H-1), 4.79 (d, 1H, $J_{13C,H}$ = 156 Hz, H-2a), 4.73 (d, 1H, $J_{13C,H}$ = 157 Hz, H-2a), 2.48−2.02 (m, 6H, H-3,3′,4a,10a,6,6′), 1.92−1.79 (m, 3H, H-4′,10′,5′), 1.36−1.22 (m, 2H, H-4,5), 1.08 (q, 1H, J = 12.4 Hz, H-10); ^{13}C NMR 144.4 (*q*, d, J = 71.7 Hz), 141.2 (*q*, d, J = 7.8 Hz), 140.5 (*q*), 130.4 (*t*), 129.0 (*t*), 125.7 (*t*), 125.3 (*t*), 110.1 (*s*), 37.9 (*s*), 35.8 (*t*), 35.6 (*t*), 30.7 (*s*), 30.6 (*s*), 30.3 (*s*), 26.0 (*s*); MS *m/z* = 199 (M^+, 100%), 184 (− $^{13}CH_2$, 8%), 143 (− $^{13}CH_2/(CH_3)_2CH$, 28%).

Photodimerization of 4,4a,5,6,10,10a-Hexahydro-2(3*H*)-methyleneanthracene (1′). (a) A solution of 440 mg of freshly chromatographed tetraene **1′** in 6 mL of benzene was sealed in a Pyrex ampule after three freeze−pump−thaw degassing cycles. The ampule was irradiated in an ice bath with a medium-pressure mercury lamp for 7 h. Filtration through a 25−50 microfilter funnel yielded **16′** as a pale yellow precipitate (46.8 mg, 10%). The benzene solution was flash chromatographed on silica gel (25 cm × 2.5 cm i.d., ether/hexane (1:3)) to give 94.5 mg of a mixture of unreacted **1′**, its dimer **16′**, and 180 mg of polymer, removable by washing the column with $CHCl_3$.

(b) A solution of 80.0 mg (0.40 mmol) of freshly chromatographed **1′-^{13}*C***, 2.0 mg of benzophenone, and 2.0 mL of benzene was irradiated as in (a). The content of the ampule was concentrated to a residue, which was triturated with 10 mL of ether, leaving a pale yellow precipitate. Filtration and washing with ether provided 66.2 mg of an impure **16′-^{13}*C*** (82.7% yield): ^{1}H NMR 5.40 (m, 4H), 5.23 (m, 2H), 2.56 (m, 2H), 1.0−2.1 (m, 24H); ^{13}C NMR 146.3 (*q*), 139.7 (*q*), 138.3 (*q*, d, J = 40 Hz), 127.7 (*t*), 122.3 (*t*), 121.2 (*t*), 44.6 (*t*), 37.8 (*t*), 36.91 (*t*), 36.88 (*s*), 35.4 (*s*), 30.3 (*s*), 30.0 (*s*), 28.3 (*s*), 27.0 (*s*); UV−vis 258 (4.35), 278 (4.40); MS *m/z* = 398 (M^+, 59%), 199 ($^1/_2M^+$, 100%).

(*R*)-4,4a*β*,5,6,10,10a-Hexahydro-10a*β*-methyl-2(3*H*)-anthracenone [(*R*)-8]. (a) In an initial experiment, the starting material was (*R*,*S*)-4,4a,5,6,7,8-hexahydro-4a*β*-methyl-2(3*H*)-naphthalenone [(***R*,*S***)-**5**], prepared according to a previously described procedure:[4] To a solution of its lithium enolate, prepared from 1.0 g of (***R*,*S***)-**5** in 10 mL of THF and lithium diisopropylamide (LDA) (from 4.8 mL of 2.5 M *n*-BuLi (2 equiv) and 2.52 mL of diisopropylamine), was added dropwise at −78 °C under a stream of N_2 over a 10 min period a solution of 0.5 mL (1 equiv) of methyl vinyl ketone (MVK) in 12 mL of anhydrous THF. After 20 min of stirring, the solution was quenched with 2.0 mL of 10% aqueous HCl, warmed to room temperature, and extracted with 10 mL of ether. Washed four times with 5 mL each of H_2O and dried over Mg_2SO_4, the ether solution was concentrated to a residue, distillation of which at 120 °C and 0.5 mmHg (Kugelrohr) afforded 0.28 g of unreacted (***R*,*S***)-**5** and, at 200 °C, 0.60 g of (*R*,*S*)-4,4a*β*,5,6,7,8-hexahydro-3-[4′-(2′-ketobutyl)]-4a*β*-methyl-2(3*H*)-naphthalenone [(***R*,*S***)-**9**] (36%): ^{1}H NMR (300 MHz) 5.67 (s, 1H), 2.60 (m, 1H), 2.45 (m, 2H), 2.25 (m, 1H), 2.15 (s, 3H), 2.10 (m, 1H), 1.90 (m, 1H), 1.80−1.55 (m, 6H), 1.30 (m, 2H), 1.25 (s, 3H). The use of 2 equiv of MVK and a 65 min reaction time gave more byproducts of condensation with two and three molecules of MKV.

A similar procedure was applied to (***R***)-**5** ($[\alpha]^{20}_D$ −229° (ethanol, *c* 1.1); ee > 99%; ^{1}H NMR 5.72 (s, 1H, vinyl H), 2.50−1.34 (m, 12H), 1.23 (s, 3H, CH_3); IR 2927, 2859, 1677, 1627, 1448, 1326, 1225, 1186, 858). A 5 g sample of (***R***)-**5**, 1.7 equiv of LDA, and 0.8 equiv of MVK (70 min reaction time) gave (***R***)-**9** in 31% theoretical yield. For the

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[25] Glatzhofer, D. T.; Longone, D. T. *Tetrahedron Lett.* **1983**, *24*, 4413−4416.

next step, a procedure of Revial and Pfau was followed.[26] A solution of 2.54 g of (***R***)-**9**, 10.0 mL of methanol, and 15 drops of 25% NaOH/MeOH, heated at 60 °C for 18 h, gave 2.42 g of impure (***R***)-**10** as a yellow oil, which was recrystallized from 5.0 mL of ether at 4 °C to give 0.9 g (second crop 0.4 g) of yellow crystals of (*R*)-(−)-4,4aβ,5,6,7,8,10,10a-octahydro-10aβ-methyl-2(3*H*)-anthracenone [(***R***)-**10**]: mp 105−106 °C; $[\alpha]^{25}_{D}$ −575° (methanol, *c* 1.967); ^{1}H NMR (400 MHz) 5.90 (s, 1H, H-9), 5.73 (s, 1H, H-1), 2.52 (m, 1H, H-3), 2.50 (m, 1H, H-4a), 2.41 (s, 1H, H-3′), 2.30 (m, 1H, H-8), 2.22 (1H, H-8′), 2.00 (m, 1H, H-4), 1.88 (m, 1H, H-4′), 1.63 (m, 5H), 1.30 (m, 3H), 1.01 (s, 3H, CH_3); ^{13}C NMR (126 MHz) 200.1, 159.3, 158.6, 122.5, 122.3, 46.0, 42.0, 38.0, 36.6, 32.7, 31.8, 30.2, 27.7, 23.2, 21.9.

A solution of 1.16 g of (***R***)-**10**, 2.65 g of chloranil, and 5.9 mg of *p*-toluenesulfonic acid in 35 mL of *tert*-butyl alcohol was boiled under reflux for 15 h. After conventional workup, recrystallization of the resulting brown oil from ether afforded 0.25 g (two crops) of (***R***)-**8**: mp 99−100 °C; $[\alpha]^{25}_{D}$ −771° (methanol, *c* 0.744).

(b) In an alternate procedure, (***R***)-**5** was first dehydrogenated by chloranil to (*R*)-(−)-4,4a,5,6-tetrahydro-4aβ-methyl-2(3*H*)-naphthalenone [(***R***)-**6**] following a procedure of Banerjee et al.,[4,27] modified by further purification of the oily product by two recrystallizations from pentane (−10 to −20 °C): 99% purity; ee > 99% (GLC); ^{1}H NMR 6.21 (m, 1H), 6.13 (dd, 1H, $J = 9.3$, 0.6 Hz), 5.65 (s, 1H), 2.66−2.58 (m, 1H), 2.43−2.35 (m, 2H), 2.30−2.24 (m, 1H), 1.92−1.82 (m, 1H), 1.79−1.74 (m, 1H), 1.62−1.50 (m, 2H), 1.16 (s, 3H); IR 3027, 2967, 2920, 1660, 1619, 1586, 1253, 1211, 872, 622.

A Michael addition of (***R***)-**6** to methyl vinyl ketone then gave the diketone (***R***)-**7**, (*R*)-(−)-4,4a,5,6-tetrahydro-3-[4′-(2′-ketobutyl)]-4aβ-methyl-2(3*H*)-naphthalenone. A solution of 5.0 g (30.8 mmol) of (***R***)-**6** in 10 mL of anhydrous THF was added dropwise to a solution of LDA (from 19.25 mL of a 1.6 M solution of *n*-BuLi and 3.43 g of diisopropylamine) at −78 °C under nitrogen. To this solution, after being stirred for 10 min, was added at −78 °C over a 10-min period a solution of 2.15 g (30.7 mmol) of freshly distilled MVK in 10 mL of anhydrous THF. After 35 min, the reaction mixture was quenched with 10 mL of 5% aqueous $NaHCO_3$, and extracted with ether (3 × 50 mL). The combined organic layers were washed with water and saturated brine, dried over Na_2SO_4, and concentrated in vacuo to a yellow oil, which was chromatographed on silica gel (elution with hexane/ethyl acetate (10:1 and 4:1)) to give recovered (***R***)-**6** (1.69 g, 34%) and diketone (***R***)-**7** (3.31 g, 66%): ^{1}H NMR 6.20 (m, 1H), 6.12 (dd, 1H, $J = 9.7$, 2.5 Hz), 5.62 (s, 1H), 2.65−2.53 (m, 3H), 2.43−2.34 (m, 1H), 2.30−2.21 (m, 1H), 2.14 (s, 3H), 2.09−2.00 (m, 1H), 1.78−1.48 (m, 5H), 1.13 (s, 3H); IR 2968, 2920, 1713, 1660, 1621, 1361, 1225, 1204, 1179, 880, 622.

A stirred methanol (50 mL) solution of (***R***)-**7** was purged of oxygen by a nitrogen stream for 15 min before the addition of 50 mg of sodium methoxide in 5 mL of methanol. After being stirred at 60 °C under nitrogen for 16 h, the cooled solution was quenched with acetic acid to pH 2−3. Removal of methanol in vacuo gave a residue which was dissolved in 100 mL of $CHCl_3$, washed with aqueous $NaHCO_3$ (2 × 20 mL), water, and brine, then dried over Na_2SO_4, and chromatographed on silica gel (hexane/ethyl acetate (6:1)) to yield (*R*)-(−)-4,4aβ,5,6,-10,10a-hexahydro-10aβ-methyl-2(3*H*)-anthracenone [(***R***)-**8**] (2.81 g, 92%). Recystallization from ethyl acetate afforded a slightly yellow material (2.30 g, 75%): mp 105 °C; $[\alpha]^{20}_{D}$ −83° (ethanol, *c* 0.109); ^{1}H NMR (toluene-d_8) 6.11 (dd, 2H, $J = 9.9$, 2.5 Hz), 6.07−6.03 (m, 1H), 5.92 (s, 1H), 5.79 (s, 1H), 2.86−2.78 (m, 2H), 2.56−2.51 (m, 1H), 2.49−2.32 (m, 2H), 2.26−2.21 (m, 2H), 2.06−2.02 (m, 1H), 1.78−1.55 (m, 4H), 1.49−1.46 (m, 1H), 1.35 (t, 1H, $J = 12.9$ Hz), 1.13 (s, 3H); IR 2920, 2852, 1647, 1578, 1561, 1323, 1201, 907, 651; UV−vis 327 (4.56); MS *m*/*z* calcd for $C_{15}H_{18}O$ 214.1358, found 214.1335 (M^+, base).

(*R*)-(−)-4,4a*β*,5,6,10,10a-Hexahydro-10a*β*-methyl-2(3*H*)-methyleneanthracene (1). This compound was prepared by a Wittig reaction as described above. From 200 mg of trienone (***R***)-8 and 680 mg of methyltriphenylphosphonium bromide, a reaction mixture (THF) was diluted with pentane, freed of a suspension by being passed through a short column of basic alumina (5 g), and concentrated in vacuo. Chromatography on basic alumina (pentane) afforded crude tetraene, which was recrystallized twice from pentane at −40 to −50 °C to give 165 mg (84%) of colorless needles: mp 83.0−83.5 °C; $[\alpha]^{20}_{D}$ −87.8° (hexane, *c* 0.109); ^{1}H NMR (toluene-d_8) 6.05 (dd, 2H, $J = 9.9$, 2.5 Hz), 5.99 (s, 1H), 5.76 (s, 1H), 5.67−5.63 (m, 1H), 4.90 (s, 1H), 4.81 (s, 1H), 2.49−2.38 (m, 2H), 2.46−2.37 (m, 1H), 2.21−2.13 (m, 1H), 1.98−1.92 (m, 2H), 1.63−1.58 (m, 1H), 1.34−1.22 (m, 4H), 1.07 (t, 1H, $J = 12.7$ Hz), 1.00 (s, 3H); IR 2926, 2849, 1607, 1579, 1448, 919, 870, 793, 645; UV−vis 323 (4.647), 308 (4.679), 294 (4.486).

In $CDCl_3$, the ^{1}H NMR spectrum reveals a mixture of **1** and its acid-catalyzed rearrangement product, (*R*)-(−)-4,4aβ,5,6,10,10a-hexahydro-2,10aβ-dimethylanthracene: ^{1}H NMR ($CDCl_3$, 300 MHz) 5.95 (m, 1H, H-3), 5.86 (s, 1H, H-1), 5.25 (s, 1H, H-9), 5.65 (m, 2H, H-7, H-8), 2.45 (m, 1H), 2.20 (m, 3H), 1.80 (s, 3H, CH_3-2), 1.67 (dd, 1H), 1.41−1.10 (m, 4H), 1.02 (s, 3H, CH_3-10a). Compound **1** not only is very sensitive to acid but also rapidly turns yellow in the presence of air. It can be stored for long periods of time at −85 °C.

Photodimerization of 1. A solution of 10 mg of **1** in 0.5 mL of toluene-d_8 was sealed in an NMR tube after three freeze−pump−thaw cycles. The tube was irradiated for 2 h at −75 °C by a Hanovia medium-pressure mercury arc lamp, and stored at −78 °C. The main product **4a** was revealed by a ^{1}H NMR (toluene-d_8) spectrum taken at −42 °C: 6.16 (dd, 2H, $J = 9.9$ and 2.0 Hz), 5.86 (s, 2H, 5.68 (m, 2H), 5.62 (s, 2H), 2.42−2.33 (m, 2H), 2.33−2.27 (m, 2H), 2.05−1.80 (m, 8H), 1.52−1.47 (m, 2H), 1.42−1.24 (m, 8H), 1.11 (t, 2H, $J = 12.8$ Hz), 1.05 (s, 6H).

After 15 min at room temperature, the ^{1}H NMR spectrum indicated a new product (**16**) and regenerated **1** in a ratio of 9:1. A similar irradiation carried out at 0 °C for 2 h afforded only **16**: ^{1}H NMR (toluene-d_8) 5.46 (d, 2H, $J = 2$ Hz), 5.29 (d, 2H, $J = 5.4$ Hz), 5.22 (d, 2H, $J = 2.7$ Hz), 2.39−2.30 (m, 2H), 2.26−2.24 (t, 2H, $J = 5.0$ Hz), 2.14−1.90 (m, 8H), 1.78 (ddd, 2H, $J = 16.4$, 5.1, and 1.9 Hz), 1.68−1.53 (m, 8H), 1.17 (ddd, 2H, $J = 25.2$, 12.6, and 5.1 Hz), 1.12 (s, 6H), 1.04 (t, 2H, $J = 11.9$ Hz); MS *m*/*z* calcd for $C_{32}H_{40}$ 424.3130 found 424.3112 (M^+, base).

A sealed glass tube containing **1** without oxygen was heated at its melting point (about 85 °C) for 10 min. A solution of the resulting solid in toluene-d_8 showed a trace of **16** by NMR. When **1** without solvent was heated at 110 °C for 16 h, 2−3% **16** was detected. Heating a 10% solution of **16** in toluene-d_8 in a sealed NMR tube at 110 °C for 16 h gave identical results. Irradiation of a thin layer of solid **1** on the glass wall of a sealed NMR tube at 0 °C for 2 h also gave 2−3% **16** along with a few percent of unidentified products.

Kinetics of Cycloreversion of 16 to 1. The rates of fragmentation of **16** to **1** as a function of temperature were determined in the manner described previously.[28] Samples of **16** in toluene-d_8 were prepared from **1** by irradiation in sealed NMR tubes at room temperature, and then heated in the vapors of solvents of appropriate boiling points.

Kinetics of Stereomutation and Cycloreversion of 4a. A solution of ~10 mg of **1** in 0.5 mL of toluene-d_8 in an NMR tube was degassed by three freeze−pump−thaw cycles and sealed under vacuum (10^{-5} mmHg). The tube was irradiated with a medium-pressure Hg lamp for 2 h at −75 °C (cooled with dry ice/isopropyl alcohol) and then stored at −85 °C. Kinetic measurements at low temperature in the range of −42.3 to −7.8 °C were conducted in a Bruker AM 500N instrument equipped with a variable-temperature unit. After the temperature was set, about 30 min was allowed for equilibrium to be reached. The sample was then moved from the dry ice/isopropyl alcohol bath to the NMR probe, 10 min being allowed for returning to equilibrium before the measurements were begun. Because **1** precipitates below −45 °C, the lowest temperature employed for kinetic studies was −42.3 °C.

The temperature unit of the NMR spectrophotometer was calibrated by a digital thermometer with a J-type thermocouple placed inside the NMR probe. A further calibration was obtained by measurements at several temperatures of the NMR spectrum of methanol in a sealed capillary placed in the NMR tube. The temperature was monitored periodically during all runs by such an internal capillary tube.

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Quantitative ^{1}H NMR spectra were measured allowing an interpulse time delay (relaxation delay and saturation period of at least 5 times the longest spin−lattice relaxation time (T_1) at each temperature). The signals used for analysis follow (in parts per million): **4a**, 5.68; **4b**, 5.91; **4c**, 5.94; **16**, 5.22; **1**, 4.90.

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Supporting Information Available: Untreated data from 17 kinetic runs between −42.3 and −7.8 °C for the system **4a**, **4b**, **4c**, **16**, and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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