Beyond Butadiene: Activation Parameters for Thermal Stereomutations and Cycloreversion of Cyclobutanes from a Photochemical Cyclodimerization of the Rigid, All-Trans Triene 4a-Methyl-2,3,4,4a,5,6-hexahydro-2-methylenenaphthalene

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Abstract: Enthalpies of stabilization of polyenyl radicals, recently determined by thermal cis–trans isomerization about double bonds, are incorporated into a model for thermal cyclodimerization (and its reverse, cycloreversion) of polyene based on the ethylene–cyclobutane paradigm. This model accommodates the butadiene–divinylcyclobutane equilibrium satisfactorily. When the model is applied to polyenes of higher order, enthalpies of activation in both directions are predicted to be strikingly lowered as the order of the polyene increases. Photochemical dimerization at –75 °C of optically pure triene (*R*)-**3** of the title, produces a *single* dimer (of three allowed), to which a cyclobutane structure in the anti and, tentatively, endo,endo configuration, (*R*,*R*)-$\mathbf{4}_{a,n,n}$, is assigned. The remarkable stereospecificity is ascribed to an intermediate excimer, in which maximum overlap and minimal steric repulsion are hypothetically achieved in either of the two incipiently anti arrangements. Irradiation of racemic (*R*,*S*)-**3** at –75 °C produces two of six possible isomers, now racemic $\mathbf{4}_{a,n,n}$ and racemic $\mathbf{4}_{a,n,x}$. Each of the photochemically favored cyclobutanes begins to equilibrate above –20 °C (very rapidly at 20 °C and above) with the other two stereoisomers in its set. From rates measured between –22.7 and 0.0 °C, Eyring parameters, $\Delta H^{\ddagger} = 21.2$ kcal/mol and $\Delta S^{\ddagger} = 2.7$ eu, are obtained. In the temperature range of 0.0 to 22.0 °C, the mixture of dimers, continuously maintained at equilibrium, undergoes thermal, [2 + 2] cycloreversion to the triene (*R*)-**3** with Eyring parameters, $\Delta H^{\ddagger} = 24.2$ kcal/mol and $\Delta S^{\ddagger} = 5.8$ eu. Although syn–anti rearrangement competes with cycloreversion in divinylcyclobutanes, the gap in enthalpy of activation between the two paths is significantly larger in these dibutadienylcyclobutanes.

A basic chapter in the chemistry of olefins is cyclodimerization to cyclobutanes, commonly effected photochemically but rarely thermally and its reverse, cycloreversion from cyclobutanes to olefins, effected almost exclusively thermally. In the conceptual scheme of Woodward and Hoffmann, this process is not concerted, except in the normally inaccessible Möbius geometry, and is likely to proceed in two steps by way of a diradical as an *intermediate*. When the olefinic component is a polyene of *n* double bonds, cyclodimerization is no longer limited in principle to the production of cyclobutanes but may generate larger rings.

The Proposition

Enthalpies of stabilization, now known for a series of polyenyl radicals extending to order 3,[1,2] can be incorporated into a simple model that leads to the prediction of some remarkably low *enthalpies* of activation for thermal cyclodimerizations of polyenes, particularly when the order of the polyene is 3 or higher.[3]

The paradigm is a two-step, thermal interconversion of two molecules of ethene[4] (cyclodimerization in the forward direction)[5] and cyclobutane (cycloreversion in the reverse).[6] For complete thermochemical description of a simple reversible system, three among the two enthalpies of formation and two enthalpies of activation are required. For the ethene–cyclobutane system, three are available. Of the factors, ΔH and $T\Delta S$, that control the position of equilibrium, enthalpy strongly favors cyclobutane by ~18 kcal/mol (the difference between the heats of formation of 2 mol of ethene and 1 mol of cyclobutane), whereas the entropy term, highly unfavorable for dimerizations in general, strongly favors ethene, the more so the higher the temperature required for a kinetically significant reaction. From known enthalpies of formation and the enthalpy of activation for the cycloreversion reported by Vreeland and Swinehart ($\Delta H^{\ddagger} = 61.8$ kcal/mol),[6c] dimerization of ethene has a calculated enthalpy of activation $\Delta H^{\ddagger} = 43.5$ kcal/mol,[4] a value which appears to have been confirmed experimentally by Quick, Knecht, and Back[5] (see Scheme I).[7]

The corresponding experimental enthalpy of formation of the rate-determining transition state is well approximated by that of the related noninteractive, 1,4-diradical, which may be modeled and defined by the addition of twice the difference in heats of formation of ethane and the ethyl radical ($\Delta\Delta H_f^{\circ} = 48.3$ kcal/mol)[8] to the heat of formation of butane. It is emphasized that the rate-determining transition state for head-to-head dimerization of two molecules of ethene or cleavage of cyclobutane is not necessarily (a) the identical state as, or the state on the way to, the antiperiplanar diradical; (b) the interconnection between the antiperiplanar and closure-capable, synclinal diradical; or (c) the transition state for closure of the latter to cyclobutane. It is assumed, however, that the rate-determining transition state, no

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

[2] Doering, W. v. E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6038–6043.

[3] The "order", *n*, defines polyenes and polyenyl radicals of *n* double bonds (see Scheme II for illustrations).

[4] Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279–5283.

[5] Quick, L. M.; Knecht, D. A.; Back, M. H. *Int. J. Chem. Kinet.* **1972**, *4*, 61–68.

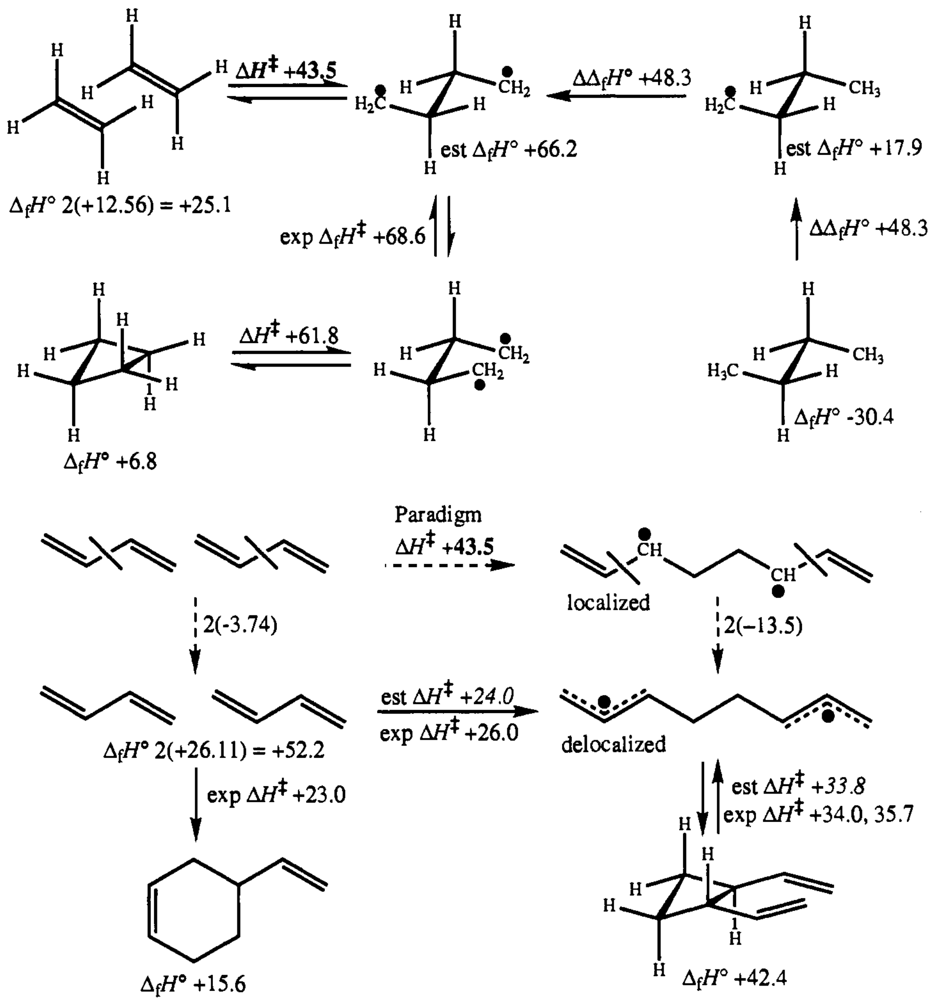
[6] (a) Genaux, C. T.; Kern, F.; Walters, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 6169–6199. (b) Butler, J. N.; Ogawa, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 3346–3348. (c) Vreeland, R. W.; Swinehart, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 3349–3353. (d) Beadle, P. C.; Golden, D. M.; King, K. D.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 2943–2947.

[7] Energies in Schemes I and II are in units of kcal/mol.

[8] Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347–1353.

0002-7863/93/1515-5414$04.00/0

Scheme I



matter to which of the three families it may belong, differs in heat of formation from the modeled antiperiplanar diradical by a tolerably small amount. This hope is quite consistent with the flatness in the potential energy surface brought to light by the theoretical calculations of Doubleday[9] and of Bernardi et al.[10]

Extension to the estimation of enthalpies of activation of cyclodimerization of higher polyenes consists accordingly in estimating the enthalpy of formation of the related noninteractive diradical. Factors that stabilize radicals are expected to enhance the rate of dimerization by lowering the enthalpy of activation and, as a consequence, are expected first, to lower the temperature associated with a reasonable rate of reaction, second, to reduce the magnitude of the $T\Delta S$ term, and third, to shift the thermodynamically controlled position of equilibrium toward the product. A remarkable illustration is the spontaneous [2 + 2] cyclodimerization of protoanemonin,[11] in which the stabilizing factor appears to be delocalization in the furanyloxy radical.

How stabilization by allylic delocalization operates can be seen in the first member of the polyene series, the cyclodimerization of butadiene. This application of the model proceeds along the lines shown in Scheme I. First, an *unperturbed* model that mimics the paradigm of ethene is created by insertion of an imaginary insulating barrier between the two double bonds of the educt, butadiene. The resulting construction is tantamount to the assertion that perturbation by a vinyl group is not different to that by a saturated alkyl group.[12] Two of these unperturbed models of butadiene are now imagined to generate an equally unperturbed, antiperiplanar diradical by head-to-head bond formation, in which absence of perturbation is symbolized again by the introduction of two barriers each between the radical and its vinylic substituent. This model is equivalent to the postulate that dimerization of butadiene, if unperturbed, has the same enthalpy of activation, 43.5 kcal/mol, as dimerization of unsubstituted ethene.[12] Removal of the barriers on both sides of the equation allows assessment of the energetic consequences of perturbation by the vinyl groups. In the educt, the effect is to lower the heat of formation of each butadiene moiety by 1 K[13] and, in this sense, to make the reaction less favorable. Removal of the barriers in the diradical lowers the enthalpy of formation of each radical by one element of allyl stabilization, SE_1, which is here taken to be 13.5 kcal/mol.[14] As summarized in Scheme I, the sum of the two perturbations results in a predicted enthalpy of activation of ≥24.0 kcal/mol for the cyclodimerization of butadiene.

This procedure implicitly involves the assumption that whatever small enthalpies separate the model diradical from the rate-determining transition state, they remain negligible or essentially

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[9] Doubleday, C., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 447–448.

[10] (a) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260–2264. (b) Bernardi, F.; Olivucci, M.; Robb, M. A. *Acc. Chem. Res.* **1990**, *23*, 405–412.

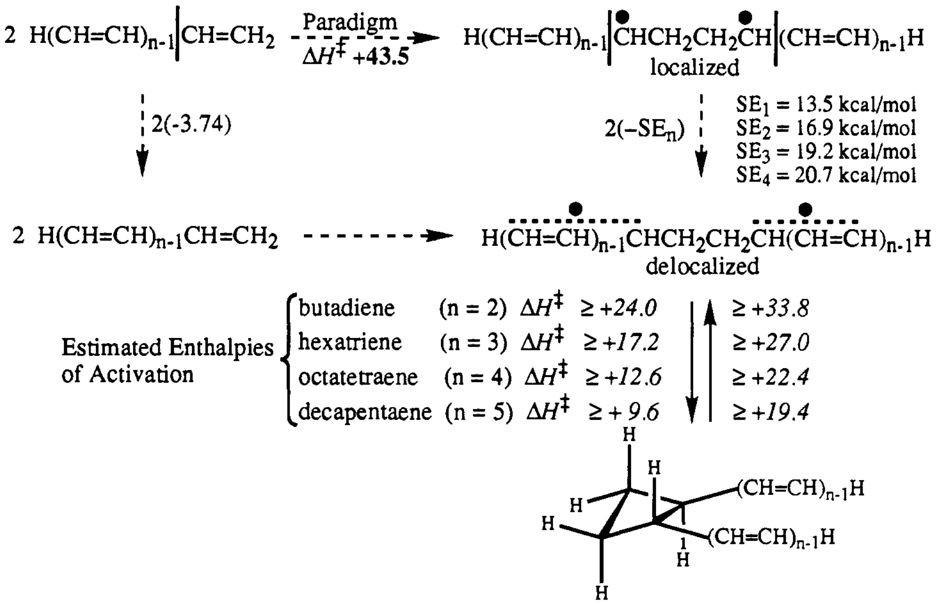
[11] (a) Asahina, Y.; Fujita, A. *Yakugaku Zasshi* **1920**, *455*, 1. (b) Moriarty, R. M.; Romain, C. R.; Karle, I. L.; Karle, J. *J. Am. Chem. Soc.* **1965**, *87*, 3251–3252.

[12] The paradigm might better have been the system propene/1,2-dimethylcyclobutane, but the kinetics and thermodynamics of the latter are less well defined. We are consoled by the independence on alkyl substitution of the heats of semihydrogenation of simple olefins.[2]

[13] K is the energy of conjugation between a pair of conjugated double bonds and is given the value 3.74 kcal/mol, as previously noted.[1] Polyenes of order n therefore have an energy of conjugation of $(n - 1)$K; note that this assertion is deplorably poorly supported by thermochemical data from polyenes of order higher than 3.

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

Scheme II



constant in proceeding from ethene to butadiene. To what extent this assumption is true is a question that becomes more interesting as the order of the polyene increases. Enthalpies of activation predicted by this procedure therefore are thought to be *minimum* values. The question will be dealt with later, but it is noted here that the enthalpy of activation predicted for the dimerization of butadiene to *trans*-1,2-divinylcyclobutane is only slightly lower than the experimental enthalpy of activation of 25–26 kcal/mol.[15,16]

Enthalpies of stabilization of polyenyl radicals have been so defined[1] that eq 1 is operative in the prediction of (presumably minimum) enthalpies of activation for head-to-head dimerization of polyenes of higher order:

$$\Delta H^{\ddagger}_{n} = \Delta H^{\ddagger}_{1} + 2\mathrm{K} - 2\mathrm{SE}_{n-1} \qquad (1)$$

The resulting values for polyenes of order 2, 3, 4 and 5, as shown in Scheme II, become surprisingly low as the order of the dimerizing polyene increases. Although there are no observations in the literature bearing on the validity of these predictions, it is perhaps relevant that both octatetraene and decapentaene are reported to polymerize spontaneously.[17]

Estimation of (minimum) enthalpies of activation for the related cycloreversions are approximated, in the absence of relevant thermochemical data, by adding the difference (9.8 kcal/mol) in heats of formation of *trans*-1,2-divinylcyclobutane (42.4 kcal/mol)[18] and twice that of butadiene (26.1 kcal/mol) to enthalpies of activation estimated for the dimerizations. The predicted value of 33.8 kcal/mol agrees very well with the experimental value of 34.0 kcal/mol for the overall transformation of *trans*-1,2-divinylcyclobutane to 4-vinylcyclohexane (~70%), *cis,cis*-1,5-cyclooctadiene (~25%) and butadiene (~5%). It also agrees well with the value of 35.7 kcal/mol calculated from the data reported for racemization of optically active *trans*-1,2-divinylcyclobutane,[19] if allowance is made for the internal rotations mandatory in this transformation.

In passing, note that dimerization within a string of double bonds in a polyene is expected to be less favorable than dimerization at terminal double bonds by 2 K. Thus, (*E*,*E*)-octa-1,3,5,7-tetraene is predicted to dimerize head-to-head with a minimum enthalpy of activation of 12.6 kcal/mol but to dimerize internally (e.g., between positions 3 and 3′) with an enthalpy of activation higher by the sum of 2K (7.5 kcal/mol) and 4.6 kcal/mol, twice the difference between SE$_3$ and SE$_2$.[20] These considerations may be relevant to the conviction voiced by Knoll and Schrock[21] that cross-linking plays a role in their *tert*-butyl-capped polyenes of high order. It is also noted that polyenes capped by an alkyl may be stabilized by as much as twice the difference in heats of hydrogenation of ethene and propene (2 × 2.8 kcal/mol) and consequently may be kinetically and thermodynamically less prone to thermal dimerization.

First Proof: Dimerization of a Triene

Compound **3**, a rigid but highly substituted polyene of order 3, has been selected as the next higher member of the series for comparison with prediction because its structure is incompatible with Diels–Alder dimerization and other, here unwanted, thermal and photochemical reorganizations.[22] In this respect, a series that begins with 3-methylenecyclohexene[23] is extended. Admittedly, the choice of a polyene other than that of the unsubstituted, all-trans parent introduces perturbations, for which neither empirical nor theoretical thermochemical compensation can be made at the present stage of experience or theory. The seemingly gratuitous perturbation by the methyl group at the bridgehead of **3**, already shown to occasion no change in the stability of the

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[15] For references and a discussion, see: Doering, W. v. E.; Franck-Neumann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833–3844.

[16] Any barrier to cleavage of diradical to monomer beyond that already present in the paradigm would be manifest as an *increase* above the predicted enthalpy of activation. Such a barrier could arise if cleavage from a closure-capable, synclinal conformation still retained a small residuum of Woodward–Hoffmann *verbot*, which would be diminished in the antiperiplanar conformation. The gain would have to exceed the cost of 2–3 kcal/mol for rotation about the C$_2$–C$_3$ bond. Partial relief in the transition state of any strain in the educt would lower enthalpy of activation below its predicted value.

[17] Spangler, C. W.; Little, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2379–2385.

[18] Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499–2521.

[19] Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899–902.

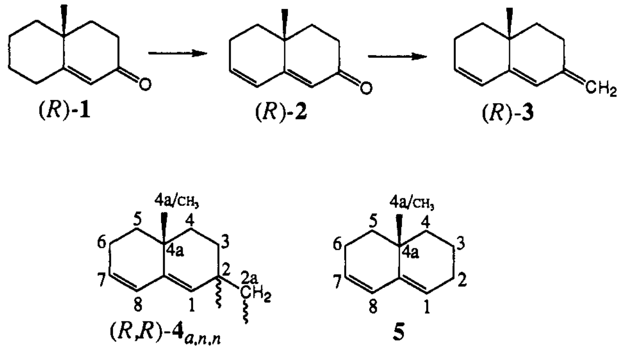
[20] Enthalpy of conjugation is expected in a first approximation to operate in a similar manner in the concerted Diels–Alder reaction, but there may be compensation to an unknown extent by an energy-lowering interaction of the external double bonds in the transition state.

[21] Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989–8004.

[22] Mulzer, J.; Kühl, U.; Huttner, G.; Evertz, K. *Chem. Ber.* **1988**, *121*, 2231–2238.

[23] Ekmanis, Juris Laimonis. Diradicals in Thermal Rearrangements: A) *cis*- and *trans*-Dispiro[5.2.5.0]tetradeca-1,8-dienes; B) Methylenecyclobutane. Ph.D. Dissertation, Harvard University, Cambridge, MA, 1976. *Diss. Abstr. Int. B* **1976**, *37*, 224B (Order No. 76-14,401).

Scheme III



pentadienyl radical,[24] is made for the ease of preparation of **3** from **2** (by an unexceptional Wittig reaction) via **1** (by dehydrogenation with chloranil)[24] (Scheme III) in both racemic (*R*,*S*) and optically active (*R*) forms. Singlet methyl signals are thereby incorporated into the NMR spectra of the products of dimerization.

Although triene **3** is predicted to dimerize easily, heating a 10% solution in benzene-d_6 (degassed and sealed under vacuum) fails to show any change after 10 days at 43 °C, after 17 h at 110.5 °C, or (neat) after 15 days at −10 °C. That thermodynamics and not kinetics is responsible for this apparent lack of reactivity is attested by the speed of cycloreversion at 20 °C of a mixture of photochemically generated dimers (*vide infra*) to monomeric triene **3**. This behavior parallels that observed by Ekmanis with 3-methylenecyclohexene: under no conditions at atmospheric pressure could dimerization be effected thermally, although either of two dimeric spirocyclobutanes generated photochemically from methylenecyclohexene could easily be reconverted by heating between 72 and 118 °C.[23]

Photodimerization

When irradiation of optically pure (*R*)-**3** is effected at −75 °C, a single dimer is produced, to which a symmetrical structure must be assigned because no more than 12 signals are observed in its ^{13}C NMR spectrum. Structures with 4-, 6-, 8-, 10-, and 12-membered rings can be considered, as well as head-to-head and head-to-tail orientations. Ring structures of 6 and 10 members do not support symmetrical structures and are therefore excluded. Structures with a *trans*,*trans*-1,5-cyclooctadiene system have steric energies, as calculated by the MM2 program available in Chem 3D Plus,[25] about 40 kcal/mol higher than those of structures containing a cyclobutane ring, which have steric energies in the range of 49–51 kcal/mol (Table I). Structures with 12-membered rings would of necessity have ^{1}H NMR signals corresponding to two tertiary allylic hydrogen atoms, regardless whether head-to-head or head-to-tail; none are observed. Examination of ^{1}H NMR and ^{13}C NMR spectra, which are collected in Table II, leads to further clarification of the structure. In the ^{13}C NMR spectrum, chemical shifts at 126.6, 128.5, and 129.6 ppm are compatible with three olefinic C(H) atoms and that at 140.6 ppm with one olefinic C(C) atom. This observation, too, is incompatible with a structure containing a 12-membered ring, which would have two carbon atoms of each type. The three olefinic Hs in the ^{1}H NMR spectrum comprise a singlet at 5.52 ppm, a multiplet at 5.63 ppm, and a doublet at 5.97 ppm fully compatible with a conjugated diene in a cyclobutane structure of type **4** (Scheme IV). Most convincing is the striking similarity in the ^{1}H and ^{13}C NMR spectra (Table II) shown by the dimer and a model compound, 4a-methyl-2,3,4,4a,5,6-hexahydronaphthalene (**5**).

Table I. Steric Energies[a] of Dimers of Ring Sizes 4, 8, and 12, Calculated by the MM2 Program[b] in Chem 3D Plus

configuration[c]	anti series	syn series
	Cyclobutane Set[d]	
endo,endo	(*R*,*R*)-$\mathbf{4}_{a,n,n}$ 49.5	(*R*,*S*)-$\mathbf{4}_{s,n,n}$ 50.9
endo,exo	(*R*,*S*)-$\mathbf{4}_{a,n,x}$ 49.2	(*R*,*R*)-$\mathbf{4}_{s,n,x}$ 50.5
exo,exo	(*R*,*R*)-$\mathbf{4}_{a,x,x}$ 50.6	(*R*,*S*)-$\mathbf{4}_{s,x,x}$ 51.1
	Cyclooctadiene Set	
endo,endo	(*R*,*R*)-$\mathbf{8}_{a,n,n}$ 88.7[c]	(*R*,*S*)-$\mathbf{8}_{s,n,n}$ 112.0
endo,exo	(*R*,*R*)-$\mathbf{8}_{a,n,x}$ 79.7	(*R*,*R*)-$\mathbf{8}_{s,n,x}$ 110.1
exo,exo	(*R*,*R*)-$\mathbf{8}_{a,x,x}$ 77.4	(*R*,*S*)-$\mathbf{8}_{s,x,x}$ 100.6
	Cyclododecatetraene Set	
endo,endo	(*R*,*R*)-$\mathbf{12}_{a,n,n}$ 64.5[c]	(*R*,*S*)-$\mathbf{12}_{s,n,n}$ 86.4
endo,exo	(*R*,*S*)-$\mathbf{12}_{a,n,x}$ 55.0	(*R*,*R*)-$\mathbf{12}_{s,n,x}$ 69.8
exo,exo	(*R*,*R*)-$\mathbf{12}_{a,x,x}$ 44.8	(*R*,*S*)-$\mathbf{12}_{s,x,x}$ 59.4

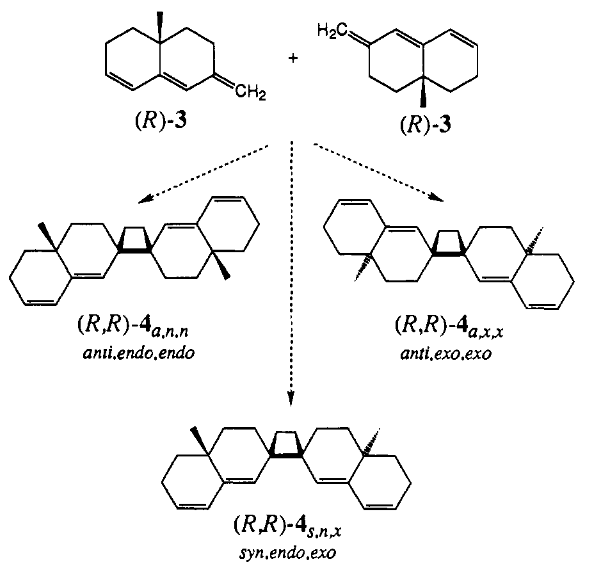
[a] In kcal/mol. [b] Torsion parameter 2.1.1.2 changed to $\nu_1 = 0.000$, $\nu_2 = 0.000$, and $\nu_3 = 1.200$ per suggestion of Professor W. R. Roth. [c] Refers to the two methyl groups. [d] The lesser value of two conformations of the cyclobutane ring.

Table II. ^{1}H NMR and ^{13}C NMR Spectra in $CDCl_3$ of Compounds **5** and (*R*,*R*)-$\mathbf{4}_{a,n,n}$ in ppm from TMS (the numbering system is shown in Scheme III)

	compound **5**[a]		compound (*R*,*R*)-$\mathbf{4}_{a,n,n}$	
postn	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
C_1	5.39	128.8 (t)[b]	5.52 (s)	129.6 (t)[b]
C_2	2.12	36.9 (s)		46.4 (q)
C_3	1.79, 1.65	25.7 (s)	2.08, 1.52	31.6 (s)
C_4	1.45, 1.32	23.2 (s)	1.42, 1.20	30.1 (s)
C_{4a}		32.2 (q)		32.2 (q)
C_{4a/CH_3}	1.01	23.1 (p)	0.95	23.1 (p)
C_5	1.45, 1.32	23.0 (s)	1.30	27.7 (s)
C_6	2.26, 2.10	37.6 (s)	2.22, 2.08	36.8 (s)
C_7	5.61	123.3 (t)[c]	5.63 (m)	126.6 (t)[c]
C_8	5.94	125.7 (t)[c]	5.97 (d)	128.5 (t)[c]
C_{8a}		140.9 (q)		140.6 (q)
C_{2a}			1.90, 1.70	34.9 (s)

[a] 4a-Methyl-2,3,4,4a,5,6-hexahydronaphthalene was prepared by Dr. Yi-qun Shi from **1** (Scheme III) by reduction of the carbonyl group and the dehydration of the resulting alcohol. [b] The letters p, s, t, and q designate primary, secondary, tertiary, and quaternary carbon atoms, respectively. [c] Assignment of C_7 and C_8 is arbitrary and can be reversed.

Scheme IV



Three configurations of a head-to-head dimer are available

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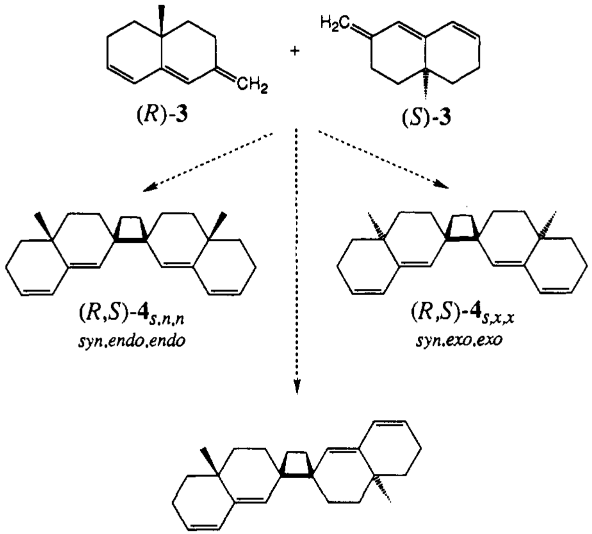
[24] Doering, W. v. E.; Shi, Y.-q.; Zhao, D.-c. *J. Am. Chem. Soc.* **1992**, *114*, 10763–10766.

[25] Cambridge Scientific Computing, Inc., Cambridge, MA 02139. Continual vigilance is needed to guard against local minima involving cyclobutane and cyclohexene conformations, *inter alia*, when applying the program.

Scheme V



(*R*)-**3** (*S*)-**3**

(*R*,*S*)-$\mathbf{4}_{s,n,n}$
syn,endo,endo

(*R*,*S*)-$\mathbf{4}_{s,x,x}$
syn,exo,exo

(*R*,*S*)-$\mathbf{4}_{a,n,x}$
anti,endo,exo

from (*R*)-**3** (Scheme IV):[26] two are symmetrical and share anti configurations, (*R*,*R*)-$\mathbf{4}_{a,n,n}$ and (*R*,*R*)-$\mathbf{4}_{a,x,x}$, in which both methyl groups are either endo or exo, and one is unsymmetrical of syn configuration, (*R*,*R*)-$\mathbf{4}_{s,n,x}$, with one methyl group endo, the other exo. With no obvious spectroscopic method by which to choose between the two symmetical configurations, the endo,endo configuration for the structure of the dimer is chosen, quite arbitrarily for the moment.[27]

Irradiation of a racemic triene, (*R*)-**3** and (*S*)-**3**, opens the way to a second set of three dimers (Scheme V). At −75 °C, a mixture of dimers showing three methyl signals in the ^{1}H NMR is obtained. One constituent is the racemic counterpart of (*R*,*R*)-$\mathbf{4}_{a,n,n}$ formed from (*R*)-**3**. The other two methyl signals are of equal area and could correspond to two syn isomers, (*R*,*S*)-$\mathbf{4}_{s,n,n}$ and (*R*,*S*)-$\mathbf{4}_{s,x,x}$, or to an unsymmetrical isomer, (*R*,*S*)-$\mathbf{4}_{a,n,x}$. Because an anti configuration was favored so strongly in the low-temperature photochemical dimerization of (*R*)-**3**, we incline toward the anti isomer (*R*,*S*)-$\mathbf{4}_{a,n,x}$ in the new set as the single source of the two methyl groups and not a fortuitous mixture of equal parts of the two syn isomers.

Thermal Reorganizations of Dimers

When (*R*,*R*)-$\mathbf{4}_{a,n,n}$ is warmed to −20 °C, three new methyl signals slowly begin to appear until over time a pseudoequilibrium is reached. On the assumption that the two remaining members of the allowed set of three have been formed, one of the new isomers appears as a singlet at 0.924 ppm relative to the methyl resonance, a singlet at 0.962 ppm, of (*R*,*R*)-$\mathbf{4}_{a,n,n}$, while that of the other appears as a doublet at 0.986 and 1.001 ppm. In the region of vinyl hydrogen atoms, two new singlets appear: one at 5.71 ppm of area 1.5 relative to that of (*R*,*R*)-$\mathbf{4}_{a,n,n}$ at 5.48 ppm and one at 5.59 ppm of relative area 0.5. Similarly, there is a new doublet centered at 6.097 ppm of area 1.5 relative to that at 6.038 ppm and a third at 5.937 of relative area 0.5. The multiplets are bunched between 5.53 and 5.63 ppm. This information is consistent with the inference that the two new isomers share the expected structures (*R*,*R*)-$\mathbf{4}_{a,x,x}$ and (*R*,*R*)-$\mathbf{4}_{s,n,x}$. It is noted without more detailed comment that other much weaker resonances can be seen in the methyl region. These do not change with time and amount to no more than 10% of the whole. In this work, such heavy reliance is placed on the NMR spectra that representative spectra have been included in the available supplementary material.

Chart I

$$\begin{tikzcd}
& \underset{\textit{anti,endo,endo}}{(R,R)\text{-}\mathbf{4}_{a,n,n}} \arrow[dl, shift left, "k_{nn/xx}"] \arrow[dr, shift left, "k_{nn/nx}"] & \\
\underset{\textit{anti,exo,exo}}{(R,R)\text{-}\mathbf{4}_{a,x,x}} \arrow[ur, shift left, "k_{xx/nn}"] \arrow[rr, shift left, "k_{xx/nx}"] & & \underset{\textit{syn,endo,exo}}{(R,R)\text{-}\mathbf{4}_{s,n,x}} \arrow[ul, shift left, "k_{nx/nn}"'] \arrow[ll, shift left, "k_{nx/xx}"]
\end{tikzcd} \quad (1)$$

$$\underset{\textit{anti,endo,endo}}{(R,R)\text{-}\mathbf{4}_{a,n,n}} \underset{[k_{xx/nn} + k_{nx/nn}] = k_r}{\overset{[k_{nn/xx} + k_{nn/nx}] = k_f}{\rightleftarrows}} \left[\underset{\textit{anti,exo,exo}}{(R,R)\text{-}\mathbf{4}_{a,x,x}} + \underset{\textit{syn,endo,exo}}{(R,R)\text{-}\mathbf{4}_{s,n,x}}\right] \quad (2)$$

$$\begin{tikzcd}
& \underset{\textit{anti,endo,endo}}{(R,R)\text{-}\mathbf{4}_{a,n,n}} \arrow[dl, shift left, "k_{nn/xx}"] \arrow[dr, shift left, "k_{nn/nx}"] & \\
\underset{\textit{anti,exo,exo}}{(R,R)\text{-}\mathbf{4}_{a,x,x}} \arrow[ur, shift left, "k_{xx/nn}"] & & \underset{\textit{syn,endo,exo}}{(R,R)\text{-}\mathbf{4}_{s,n,x}} \arrow[ul, shift left, "k_{nx/nn}"']
\end{tikzcd} \quad (3)$$

$$\begin{tikzcd}
\left[\underset{\textit{anti,endo,endo}}{(R,R)\text{-}\mathbf{4}_{a,n,n}}\right. \arrow[r, shift left] & \underset{\textit{anti,exo,exo}}{(R,R)\text{-}\mathbf{4}_{a,x,x}} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift right, "k_{-d}"'] & \left.\underset{\textit{syn,endo,exo}}{(R,R)\text{-}\mathbf{4}_{s,n,x}}\right] \arrow[l, shift left] \\
& 2\ (R)\text{-}\mathbf{3} \arrow[u, shift right, "(k_d)"'] &
\end{tikzcd} \quad (4)$$

Rates of establishment of equilibria among the three optically active dimers starting from (*R*,*R*)-$\mathbf{4}_{a,n,n}$ can be followed conveniently at −22.7 and 0.0 °C. The competing reaction of cycloreversion to the triene (*R*)-**3** is so much slower that the kinetics can be treated as a collection of reversible first-order processes in neglect of cycloreversion without significant insult to accuracy. Kinetic model 1, as outlined in Chart I, cannot be resolved with acceptable accuracy because only (*R*,*R*)-$\mathbf{4}_{a,n,n}$ of the three isomers is available to serve as starting material. Of the six specific rate constants, $k_{nn/xx}$ and $k_{nn/nx}$ are well determined, $k_{xx/nn}$ and $k_{nx/nn}$ less well, and $k_{xx}/_{nx}$ and $k_{nx/xx}$ not at all well! The experimental data, available as supplementary material in Tables S1 and S2, can be handled in terms of the more limited model 2 of a simple reversible reaction, as if the sum of (*R*,*R*)-$\mathbf{4}_{a,x,x}$ and (*R*,*R*)-$\mathbf{4}_{s,n,x}$ was a single entity. The resulting rate constants and Arrhenius parameters are collected in Table III.

Although the full scheme 1 is underdetermined, a limited scheme (3) is applied to the data at −22.7 °C to extract useful values for the four rate constants for the interconversions of (*R*,*R*)-$\mathbf{4}_{a,n,n}$ and (*R*,*R*)-$\mathbf{4}_{a,x,x}$ and of (*R*,*R*)-$\mathbf{4}_{a,n,n}$ and (*R*,*R*)-$\mathbf{4}_{s,n,x}$. The results are recorded in Table III.

Cycloreversion of dimer to triene **3** is slow at 0.0 °C and quite rapid at 20 °C. At the higher temperatures, rates of interconversion among the possible configurations are fast enough relative to cycloreversion to maintain the equilibrium ratios. At 0 °C,

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[26] Isolation of the dimer in crystalline form having so far been elusive, determination of structure by X-ray crystallography has not been possible. Structures corresponding to head-to-tail dimerization are not seriously considered on the mechanistic ground that likely intermediate diradicals would be composed of an unstabilized primary radical and a stabilized pentadienyl radical instead of two pentadienyl radicals.

[27] The high degree of stereoselectivity in low-temperature irradiation is quite remarkable. Speculatively, a head-to-head excimer is proposed as an immediate precursor to dimerization. In such an excimer, the two triene moieties are expected to maximally overlap in parallel fashion. The weakness of bonding in such complexes should leave them quite sensitive to differences in steric repulsion. Syn configurations appear sterically very crowded in Dreiding models in comparison to anti, but it is not obvious why, of methyl groups, endo or exo, one is so strongly preferred over the other. Completion of the dimerization in an allowed concerted mechanism should preserve whatever stereochemistry is favored in the excimer. Completion by stepwise formation, first, of a head-to-head bond via a diradical would have to be followed by formation of a second more rapidly than the occurrence of internal rotation, a process by which equilibrium among conformers leading to the other two allowed stereoisomers would be established.

Table III. Kinetics of Thermal Establishment of the Equilibrium in Toluene-d_8 at −22.7 and 0.0 °C among the Three Optically Active Isomers Starting from (R,R)-$\mathbf{4}_{a,n,n}$: Specific Rate Constants and Activation Parameters

T, °C	k_f[a–c]	k_r[a–c]
−22.7 ± 0.1[b]	6.5 ± 0.4	4.0 ± 0.6
0.0 ± 0.1	244 ± 5	136 ± 4
	Arrhenius Plot [$1/T$ vs $\log k$][d,e]	
E (kcal/mol)	21.7 ± 0.6	21.05 ± 1.0
$\log A$	13.75 ± 0.4	12.97 ± 0.8
	Eyring Parameters[f]	
$\Delta H^{\ddagger}$ (kcal/mol)	21.2 ± 0.6	20.5 ± 1.0
$\Delta S^{\ddagger}$ (eu)	2.7 ± 1.7	−0.9 ± 4.0

[a] $k_f = [k_{nn/xx} + k_{nn/nx}]$ and $2k_r = [k_{xx/nn} + k_{nx/nn}]$ based on data available as supplementary material in Tables S1 and S2, in units of 10^{-6} s^{-1}. [b] Double standard errors for 90% confidence limits. [c] Values for $k_{nn/xx} = 3.8 \pm 0.5$, $k_{nn/nx} = 2.8 \pm 0.5$, $k_{xx/nn} = 4.1 \pm 1.3$, and $k_{nx/nn} = 3.9 \pm 1.7$ at −22.7 °C can be extracted according to scheme 3, Chart I. [d] By the Arrhenius (or van't Hoff) expression. [e] Uncertainties are estimated by calculating activation parameters from the specific rate constant at the lower temperature plus its standard deviation and from the specific rate constant at the higher temperature minus its standard deviation and vice versa. Reported "±" is half the difference. [f] Calculated at −11.4 °C.

Table IV. Kinetics of Thermal Cycloreversion of the Equilibrium Mixture of the Six Racemic and Three Optically Active Dimers **4** to (R,S)-**3** and (R)-**3**, Respectively, in Toluene-d_8: Specific Rate Constants and Activation Parameters

T, °C	k_{-d}[a]	k_{-d}[b]
0.0 ± 0.1	4.50 ± 0.06	4.69 ± 0.39
9.0 ± 0.5	19.14 ± 0.4	18.04 ± 0.7
22.0 ± 0.1	135.0 ± 2.3	139.3 ± 4.2
	Arrhenius Plot [$1/T$ vs $\log k$][c]	
E_a (kcal/mol)	24.8 ± 0.2[d]	24.8 ± 0.9
$\log A$	14.47 ± 0.3	14.40 ± 0.0
	Eyring Parameters[e]	
$\Delta H^{\ddagger}$ (kcal/mol)	24.3 ± 0.2	24.2 ± 0.9
$\Delta S^{\ddagger}$ (eu)	5.8 ± 0.3	5.7 ± 3.0

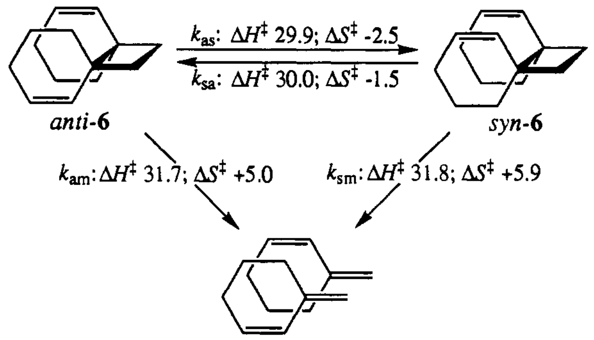
[a] Racemic dimers based on data in Tables S3 and S4; $\times 10^{-6}$ s^{-1}. [b] Optically active dimers based on data in Table S3; $\times 10^{-6}$ s^{-1}. [c] By linear regression of the Arrhenius expression. [d] Double standard errors for 90% confidence limits. [e] Calculated at 11.0 °C.

there is also no observable change in equilibrium ratios, a behavior consistent with no great differences in rates of decomposition among the various stereoisomers. At the end of a typical run, no detectable amount of dimers remains. The kinetics of cycloreversion can be handled as a simple, first-order irreversible reaction as in scheme 4 of Chart I. Specific rate constants and activation parameters are based on data available in Tables S4 and S5 as supplementary material and are summarized in Table IV.

Conclusions

The prediction that thermal dimerization of a triene would occur more rapidly than that of a diene in a measure related to the stabilization energies of pentadienyl and allyl radicals, respectively, could not be addressed directly because of thermodynamically unfavorable equilibria between monomers and dimers. The related reverse of dimerization, cycloreversion, has provided confirmation of the prediction. Comparison with 3-methylenecyclohexene and its dimers[23] is more appropriate than comparison with butadiene and its dimeric cyclobutanes, owing to several competing reactions open to butadiene. Relevant results of the investigations of Ekmanis are shown in Scheme VI. Noteworthy is the lower enthalpy of activation (30.0 kcal/mol) for syn–anti interconversion than those for rearrangement and racemization of 1,2-*trans*-divinylcyclobutane (34.0 and 35.7 kcal/mol, respectively).[19] The difference is reasonably ascribed to the extra strain energy in *anti*-**6** (4.4 kcal/mol) revealed by comparison of heats of formation calculated by MM2-ERW[28] and by Benson's group's equivalent values.[29] A similar difference is seen in the cycloreversion reactions.

Scheme VI



The enthalpy of activation for interconversion of (R,R)-$\mathbf{4}_{a,n,n}$ is lower than that for interconversion of *anti*-**6** and *syn*-**6** by 8.8 kcal/mol. Agreement with the predicted difference of 6.8 kcal/mol [Scheme II: $2(SE_2 - SE_1)$] is deemed very good, accepted that the strain energies in compounds **4** are likely to be somewhat larger than those in compounds **6**. Similarly, cycloreversions of compounds **4** have an enthalpy of activation lower than that of compounds **6** by 7.5 kcal/mol.

How much faster interconversion is than cycloreversion in compounds **4** is an immediately striking feature: at 0.0 °C, the specific rate constant k_f is 52 times larger than k_{-d}. By contrast, in the methylenecyclohexene system, that ratio is 0.7! Between the two systems, differences in enthalpies of activation in the two reactions are in the appropriate direction, −3.5 versus −1.8 kcal/mol, respectively, but these differences are too close to experimental uncertainties to conclude confidently that the surprise has its origin in the enthalpy term. Nonetheless, there is a suggestion of a trend in the series cyclobutane,[30] divinylcyclobutane, and now dibutadienylcyclobutane. If cleavages of intermediate tetramethylene diradicals are more favorable in antiperiplanar conformations, then they would all have in common an incremental barrier to rotation of 2–3 kcal/mol. From this work, there remains the titillating suggestion that a further incremental barrier to cleavage may be coming from the increase in stabilization energy of the individual pentadienyl radicals comprising the diradical. Whether stereomutations occur at the stage of the hypothetical, initial synclinal diradical or occur only after arrival at the antiperiplanar conformation is a point to be resolved. It is clear, however, that separation between stereomutation and cycloreversion has been noticeably enhanced.

In this system and the Ekmanis system, entropies of activation for the stereoisomerizations fall in the range of −2.5–2.7 eu. That range seems compatible with a rate-determining step involving transition states proceeding toward synclinal diradicals. Entropies of activation for the cycloreversions fall in the range of 5.0–5.9 eu. That range seems compatible with a rate-determining transition state proceeding from diradicals in preequilibrium toward dissociated monomeric polyenes.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) instrument. Chemical shifts are reported from CDCl$_3$ (7.24) or toluene-d_8 (7.00) in ppm (δ) with respect to TMS. Differentiation among carbon

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(28) We are grateful to Professor W. R. Roth for this calculation.

(29) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 272.

(30) Cannarsa, Michael, J. The Synthesis and Thermolysis of Stereospecifically Labelled 1,2,3,4-Cyclobutanes (Professor Melvin J. Goldstein, Research Director). Ph.D. Dissertation, Cornell University, Ithaca, NY, 1984. *Diss. Abstr. Int. B* 1984, *45*, 1468B (Order No. 84-15,310).

types was by ^{13}C NMR based on the DEPT method. Spin–lattice relaxation times (T_1) were determined by the inversion recovery method on vacuum-sealed solutions in toluene-d_8 or benzene-d_6. Melting points are not corrected. A 450-W, medium-pressure Hanovia Hg-lamp, Model 679A36, was used for the photochemical reactions.

4a-Methyl-2,3,4,4a,5,6-hexahydro-2-methylenenaphthalene (3). The starting ketone 4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (**1**) was prepared according to Heathcock et al. by acid-catalyzed Robinson annulation with the modification that the initially isolated product, which turned out to be a mixture of desired ketone **1** and uncyclized diketone, was treated a second time with concentrated H_2SO_4 in benzene.[31] Conversion to 4a-methyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (**2**) followed the procedure of Banerjee et al.:[32] 48% of theoretical yield, 95.5% of purity by GC (HP 5890a gas chromatograph, J&W Scientific DB-1701 capillary column, 30 m × 0.54 mm), and ^{1}H NMR identical to that reported.[24]

Preparation of triene **3** was modeled after a general Wittig procedure.[33] *n*-BuLi (138.2 mL of a 2 M solution in pentane, 276.3 mmol; Aldrich) was added over 65 min to methyltriphenylphosphonium bromide (91.4 g, 255.8 mmol; Aldrich, 98%) in 740 mL of dry THF at 0 °C under argon, and the solution was stirred at 0 °C for 45 min. A solution of **2** (25.0 g, 154.1 mol) in 175 mL of dry THF was then added to the ylide over a period of 55 min at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 17 h. Concentration under vacuum afforded a brown, gummy residue, which was washed repeatedly with hexane. The combined organic washings were dried over K_2CO_3 and concentrated to yield 23.3 g of a yellow liquid. Vacuum distillation provided **3**: 21.0 g in 80% of theoretical yield; 94% of purity by GC (*vide supra*); bp 57–59 °C at 0.25–0.50 mmHg. Careful vacuum fractional distillation afforded **3** of 97% purity: bp 50 °C at 0.62 mmHg; mp –11 to –10 °C. ^{1}H NMR (toluene-d_6, 500 MHz, referenced to the CH_2 signal of 18-crown-6 ether at 3.52 ppm): 6.20 (d, 1 H, =CH endocyclic), 5.88 (s, 1 H, =CH endocyclic), 5.67 (br t, 1 H, =C*H*CH_2), 4.90 (s, 1 H, =CH exocyclic), 4.82 (s, 1 H, =CH exocyclic), 2.57 (t, 1 H, CHC=), 2.30 (d, 1 H, CHC=), 2.24–2.13 (m, 1 H, CHC=), 1.98 (m, 1 H, CHC=), 1.46–1.36 (m, 2 H, CH_2), 1.35–1.29 (m, 2 H, CH_2), 0.98 (s, 3 H, CH_3).

Optically active (*R*)-**3** was prepared by the same sequence from (*R*)-4a-methyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone ((*R*)-**1**) (4.5 g, 27.4 mmol; Fluka, >98%; mp 16–17 °C; $[\alpha]^{20}{}_D = -210\pm10°$ [neat]), $[\alpha]^{27}{}_D = -204°$ (c = 1.20, ethanol). (*R*)-**1** was also prepared according to the procedure of Revial and Pfau.[34] In the last step C, the crude product was distilled under reduced pressure to give 91.9 g of a slightly yellow oil: bp 110–120 °C (5 mmHg); 81.7% of purity by GC; $[\alpha]^{25}{}_D = -134°$ (c = 0.956, ethanol). Based on the given $[\alpha]^{20}{}_D = -219°$ (c = 1.00, ethanol), the calculated ee for the condensation is 75% ([134/219][100/81.7]) not 91% as indicated in Note 6 of ref 34. Enantiomerically pure (*R*)-**1** was obtained after three recrystallizations from pentane: 17.5 g of a slightly yellow oil; 96.3% of purity by GC (complete removal of impurity, as reported, required purification by preparative GC); $[\alpha]^{25}{}_D = -210.2°$ (c = 0.696, ethanol), corresponding to an optical purity of 99.7%.

Conversion of (*R*)-**1** to (*R*)-4a-methyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone ((*R*)-**2**) was effected as above: from 4.5 g of ketone; 1.82 g as a pale yellow oil, 99% by GC; mp 15 °C; $[\alpha]^{27}{}_D = -478°$ (c = 1.30, CCl_4). ^{1}H NMR ($CDCl_3$, 400 MHz): 6.28–6.22 (m, 1 H, =CH), 6.18–6.12 (dd, 1 H, =CH), 5.67 (s, 1 H, =CH), 2.72–2.58 (m, 1 H, CHC=), 2.49–2.23 (m, 3 H, CH_2CO, CHC=), 1.95–1.75 (m, 2 H, CH_2), 1.68–1.50 (m, 2 H, CH_2), 1.17 (s, 3 H, CH_3).

Conversion to (*R*)-4a-methyl-2,3,4,4a,5,6-hexahydro-2-methylenenaphthalene ((*R*)-**3**) yielded an orange oil (1.46 g), which was purified by vacuum fractional distillation: 97% by GC; $[\alpha]^{25}{}_D = -400°$ (c = 0.4, CCl_4).

Heating a 10% solution of triene **3** in benzene-d_6 (degassed and sealed under vacuum) for 10 days at 43 °C or for 17 h at 110.5 °C occasioned no change. Neat *rac*-**3** (degassed and sealed under vacuum) was held at –10 °C for 15 days but also suffered no change.

Photodimerization of *rac*-3. A solution of racemic triene **3** (88.5% of purity, 113.4 mg, 0.63 mmol), 18-crown-6 (8.7 mg, 0.033 mmol; Aldrich, 99.5+%; as internal standard), benzophenone (4.7 mg, 0.026 mmol), and toluene-d_8 (0.8 mL; Isotec, 99.96 atom % D) was divided into two equal portions; each was placed into NMR tubes and degassed and sealed under vacuum. The samples were photolyzed with an Hanovia medium pressure mercury arc lamp for 2 h at 0 °C and then stored at –78 °C. The very complicated ^{1}H NMR spectrum is the same as that from another irradiation in toluene-d_8 without benzophenone as sensitizer.

The mass spectrum was obtained by rapidly transferring small samples to glass capillary tubes by means of a syringe. The capillary tubes were cooled to –75 °C, sealed, and stored at –15 °C until use. The tubes were cut, placed in the sample probe of a JEOL Model AX-505H mass spectrometer, and inserted part way into the ion source. When most of the toluene had been evaporated and the pressure was again 10^{-6} Torr, the probe was fully inserted into the ion source (150 °C) and data were collected. The mass spectrum was independent of the energy of the ion source over the range of 20–70 eV: m/e (rel intensity) calcd for $C_{24}H_{32}$, 320; found 320 (7.7), 305 (1.2), 160 (100.0), 145 (66.0).

Photodimerization of (*R*)-3. A solution of 11.90 mg of (*R*)-**3** in 0.40 mL of benzene-d_6 was sealed in an NMR tube after three freeze–pump–thaw cycles under vacuum and irradiated for 2 h at 5 °C to afford a product, the ^{1}H NMR spectrum of which, taken at 10 °C, showed four methyl signals: 1.001 ppm (relative area, 0.5); 0.986 (0.5); 0.962 (1.0); 0.924 (1.0).

The product of a similar irradiation of 19.45 mg of (*R*)-**3** in 0.40 mL toluene-d_8 for 1.5 h at –75 °C (cooled with dry ice/isopropyl alcohol), when examined at –30 °C, revealed only one major methyl signal in the ^{1}H NMR spectrum and a ^{13}C NMR spectrum with only 12 lines. ^{1}H NMR (–30 °C, toluene-d_8, 500 MHz, assignment based on decoupling experiments): 6.04 (d, J = 9.76 Hz, H-8, 2 H), 5.55 (m, H-7, 2 H), 5.46 (s, H-1, 2 H), 2.08 (m, H-6, H-3, 4 H), 1.89 (m, H-6′, H-2a, 4 H), 1.70 (m, H-2a′, 2 H), 1.52 (m, H-3′, 2 H), 1.42 (m, H-4, 2 H), 1.31 (m, H-5,5′, 4 H), 1.20 (m, H-4′, 2 H), 0.96 (s, CH_3, 6 H). ^{13}C NMR (–30 °C, toluene-d_8, 125.8 MHz): 140.9 (q), 130.1 (t), 129.5 (t), 126.7 (t), 46.8 (q), 37.5 (s), 35.6 (s), 32.6 (q), 30.7 (s), 28.3 (s), 23.6 (s), 23.0 (p).[35]

When an NMR tube containing the mixture of the three optically active dimers in approximate ratio 1:1:1 was augmented by an equal molar amount of monomer and irradiated at –75 °C for 1.5 h, a low-temperature ^{1}H, NMR spectrum revealed that the monomer had disappeared and only the methyl peak of the single, "low-temperature" dimer had increased.

Kinetics of Stereomutation and Cycloreversion of Racemic and Optically Active 4. Measurement of rates generally followed the previously published procedure.[1] Analysis was by ^{1}H NMR spectroscopy on a Bruker AM-500 instrument.

(a) (*R*,*R*)-$4_{a,n,n}$ (Tables S1 and S2). A solution of ca. 10 mg of (*R*)-**3** in 0.40 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. For the kinetic measurements at 0.0 °C, cooling was effected with an ice-water bath. For kinetics at –22.7 °C, the sample was kept in a Dewar flask containing a bath consisting of liquid and solid *N*,*N*-dimethylacetamide (mp –22.7 °C). The temperature in the dewar remained constant for 8 h when it was kept in a refrigerator at –10 °C. After each 6–8-h period, the sample was removed to a dry ice/isopropyl alcohol bath and kept there both before and after an NMR measurement conducted at a temperature below –30 °C. Until the next period of heating at –22.7 °C, the sample was kept in the freezer at –75 °C. Temperatures during all kinetic runs were monitored before and after every NMR measurement with a thermocouple thermometer, Model No. 8528-10, DIGI-Sence. The NMR measurement was made only after the instrument had cooled down and stabilized at or below –30 °C. The sample was protected from light throughout kinetic measurements.

The sample was analyzed by means of methyl signals of the dimer and monomer between 1.1 and 0.9 ppm (for (*R*)-**3**, T_1 = 1.60 ± 0.05 s; for (*R*,*R*)-$4_{a,n,n}$, T_1 = 0.72 ± 0.04 s; for (*R*,*R*)-$4_{a,x,x}$, T_1 = 0.65 ± 0.05 s; for (*R*,*R*)-$4_{a,n,x}$, T_1 = 0.74 ± 0.03 s). A relaxation delay and a saturation period five times the longest T_1 of the concerned protons, namely 10 s, were taken between pulses. Accumulation of 24 FIDs with a 90° pulse, which required ca. 6 min, gave a spectrum with a satisfactory signal to noise ratio. No cleavage to **3** was observed during the measurement. Relative molar concentrations were evaluated from the relative areas of the single peaks associated with (*R*,*R*)-$4_{a,n,n}$ and (*R*,*R*)-$4_{a,x,x}$, the sum of the two peaks associated with (*R*,*R*)-$4_{a,n,x}$, and *twice* the single peak of (*R*)-**3**.

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[31] Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. *Tetrahedron Lett.* **1971**, 4995–4996.

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

[33] Leopold, E. J. *Organic Synthesis* **1986**, *64*, 164–174.

[34] Revial, G.; Pfau, M. *Organic Synthesis* **1991**, *70*, 35–45.

[35] The letters p, s, t, and q abbreviate primary, secondary, tertiary, and quaternary carbon atoms, respectively.

(b) *rac*-4 at 0.0, 9.0, and 22.0 °C (Tables S3 and S4). A relaxation delay and a saturation period five times the longest T_1s of the concerned protons were taken between pulses. It was 20 s for dimer, tetraene, and methylene protons of 18-crown-6 ether. Accumulation of about 8 FIDs with a 90° pulse, which required ca. 3 min, gave a spectrum with a satisfactory signal to noise ratio. No cleavage was observed during the measurement. The area of the methylene signals at 3.52 ($T_1 = 0.95 \pm 0.01$s) was used as standard. All the areas were measured by computer integration of the spectra. The integral of one of the exocyclic methylene proton signals of the triene was compared to the CH_2 proton signal of 18-crown-6 for determining the appearance of a triene. Concentrations of dimer and triene vs time were calculated, converted to percentages, and used to calculate first-order specific rate constants by the usual expression. Analysis of the data, available as supplementary material in Table S4, from three experiments at 22 °C gives a mean rate constant of $1.35 \pm 0.023 \times 10^{-4}$ s^{-1}. The runs at 0.0 °C (ice–water bath) and at 9.0 °C (cooling in an NMR instrument) were conducted in similar fashion, the data being available as supplementary material in Tables S3 and S4.

(c) Optically Active 4 at 0.0, 9.0, and 22.0 °C (Table S5). Experiments on the equilibrium mixture of the three optically active dimers **4** were conducted in a similar manner.

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Supplementary Material Available: Unprocessed data from the study of the kinetics of thermal stereomutation and cycloreversion of **4** listed in Tables S1–S5 and 12 critical ^{1}H and ^{13}C NMR spectra with appropriate captions (18 pages). Ordering information is given on any current masthead page.