Thermal Reactions of *anti*- and *syn*-Dispiro[5.0.5.2]tetradeca-1,8-dienes: Stereomutation and Fragmentation to 3-Methylenecyclohexenes. Entropy-Dictated Product Ratios from Diradical Intermediates?

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Received November 30, 2000

Abstract: A series of cyclobutanes substituted 1,2- by polyenes of increasing radical-stabilizing power has been investigated to test the proposition that stabilization energies obtained independently from apposite, cis,-trans geometric isomerizations can be successfully transferred to another system, in this paper, cyclobutanes. The first member of the series, 3-methylenecyclohexene (**1**), is photodimerized to *anti*- and *syn*-dispiro[5.0.5.2]-tetradeca-1,8-dienes (*anti*-**2** and *syn*-**2**), which undergo stereomutation (stereochemical interconversion) and cycloreversion (fragmentation) to **1** when heated in the range 72.1−118.2 °C: *anti*-**2** → *syn*-**2**, $\Delta H^{\ddagger} = 30.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 0.2$ cal mol^{-1} K^{-1}; *anti*-**2** → **1**, $\Delta H^{\ddagger} = 32.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = +8.0$ cal mol^{-1} K^{-1}. Agreement with an enthalpy of activation predicted by assuming full allylic stabilization in a hypothetical diradical intermediate is good. An example of further activation by a radical-stabilizing group is manifested by the ∼20 000-fold acceleration in rate shown by the system 1-phenyl-3-methylenecyclohexene (**3**) and *anti*- and *syn*-2,9-diphenyldispiro[5.0.5.2]tetradeca-1,8-dienes (*anti*-**4** and *syn*-**4**), measured, however, only at 43.6 °C. In both systems **2** and **4**, volumes of activation for stereochemical interconversion and cycloreversion have been determined and found to be essentially identical within experimental uncertainties, $\Delta V^{\ddagger} = +10.2 \pm 1.0$ and $+12.6 \pm 1.4$ cm^3 mol^{-1}, respectively (weighted means). These strongly positive values are consistent with the rate-determining step being the first bond-breaking, while the near identity of the volumes of activation argues against the indispensable second bond-breaking being a determining factor in fragmentation. These results are consistent with the theoretically based construct of Charles Doubleday for the paradigm, cyclobutane, in which the ratio between two channels of exit from a "generalized common biradical" is not controlled by enthalpy *and* entropy, as in the transition state model, but by *entropy* alone.

Introduction

Dealing mechanistically with not-obviously-concerted thermal rearrangements that involve competitive formation of two or more products has a long and frustrating history. The pressing question in mechanistic thinking about such "no-mechanism" systems has centered about the nature and role of hypothetical diradical intermediates. Expressed specifically in terms of the archetypal system, cyclobutane and two molecules of ethylene, two questions may be asked. Should bond-breaking (or bond-making in the reverse direction) lead to barrier-protected, diradical-like tetramethylenes in gauche and antiperiplanar conformations, each capable of further internal rotation prior to cleavage to two molecules of ethylene, or to closure to cyclobutane? Or should the elements of bond-breaking, bond-making, and internal rotations be combined into competing "concerted" processes, some "allowed", some "forbidden"? Theoretical efforts to elucidate the thermal behavior of the pristinely unsubstituted archetypal cyclobutane in the gas phase have been extensive.[1−4] At the experimental level, intrepid purists have explored these questions with deuterium as a minimal perturbation,[5−8] while soldiering pragmatists have introduced more drastic perturbations in the hope of achieving answers.

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10.1021/ja004128s CCC: $20.00
Published on Web 05/16/2001

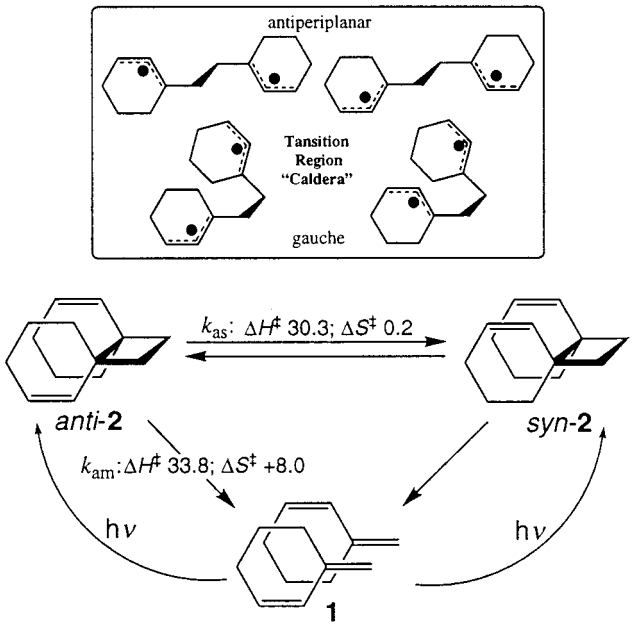

Figure 1. Activation parameters for stereomutation and fragmentation in the system **1**/**2** are given as $\Delta H^{\ddagger}$ in kilocalories per mole and $\Delta S^{\ddagger}$ in calories per mole per kelvin. Conformations of the diradical intermediates are depicted at the top.

Among well-studied examples are the systems 1,3-butadiene/1,2-divinylcyclobutane and piperylene/1,2-dipropenylcyclobutane.[9] Both are representative of dienes free to assume cisoid or transoid conformations ad libitum, and both encompass several reaction channels in the forward direction, including dimerization to cyclobutanes, cyclooctadienes, and vinylcyclohexenes, as well as stereomutation and cycloreversion of the resulting cyclobutanes. Mechanistic studies understandably have been complicated.

In the present study, a larger but chemically simpler diene is examined: 3-methylenecyclohexene (**1**) and two derived [2 + 2] photodimers, *anti*- and *syn*-dispiro[5.0.5.2]tetradeca-1,8-diene (*anti*-**2** and *syn*-**2**). A close relative included in this study involves further substitution by the strongly radical-stabilizing phenyl group: system **3**/**4** consisting of 1-phenyl-3-methylenecyclohexene (**3**) and *anti*- and *syn*-2,9-diphenyldispiro-[5.0.5.2]tetradeca-1,8-diene (*anti*-**4** and *syn*-**4**). The butadiene group in these semicyclic dienes being strictly confined to a transoid conformation, dimers of the vinylcyclohexene and 1,5-cyclooctadiene types are precluded on thermodynamic grounds owing to the energetic cost of having trans double bonds in small rings. Permitted reactions are limited to stereochemical interconversion (stereomutation) and cycloreversion (fragmentation) (Figure 1), just as they are in the archetype.

Results

For the preparation of **1** in quantity, the method of Blomquist et al.[10] involving the Prins reaction of cyclohexene and formaldehyde followed by flow pyrolysis of the resulting 3-acetoxymethylcyclohexene[11] is preferred to the reaction of the Wittig reagent from methyl bromide with cyclohex-2-enone, or that from 3-bromocyclohexene with formaldehyde.[12] Although yields are low in all procedures, the product of the flow pyrolysis can be purified by distillation (99%), whereas that from the other two methods requires laborious enrichment by preparative GLC to achieve no better than 90% purity.[13,14]

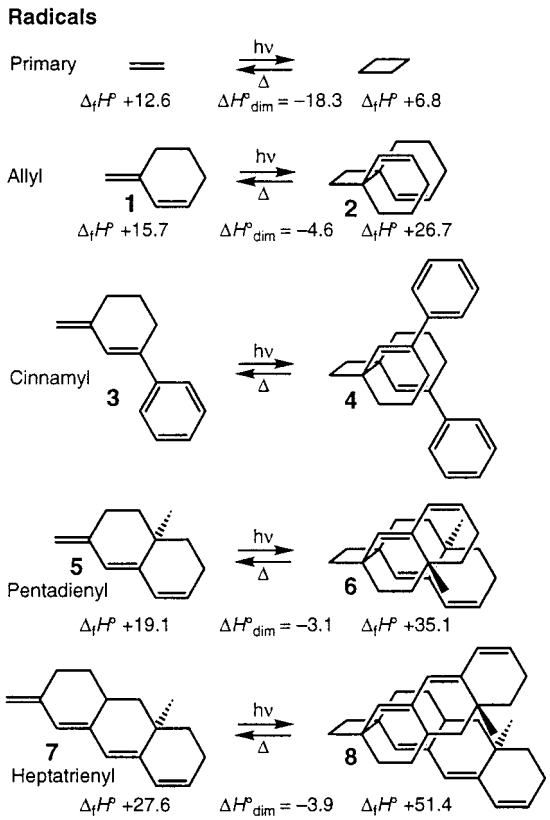

Figure 2. Polyenes and their corresponding *anti*-cyclobutane dimers (but not *syn*-) are shown, along with heats of formation and derived heats of dimerization (kcal mol^{-1}) as calculated by using Roth's molecular mechanical program, MM2EVBH.

Thermal dimerization of **1** has been attempted in vain at atmospheric pressure and temperatures where the related dimeric cyclobutanes **2** (vide infra) undergo cycloreversion.[15] The unfavorably large entropy of a bimolecular reaction appears to have overwhelmed a favorable difference in enthalpy of formation,[16] which, however, has been made less so than in the archetype by a substantial enthalpy of conjugation in the monomer (∼7.5 kcal mol^{-1}), and what appears to be repulsive strain energy in the tetrasubstituted dimer (∼6 kcal mol^{-1}), as calculated by the force field program MM2EVBH (see Figure 2).[17b,18]

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(13) A formal preparation of **1** exists in the base-catalyzed equilibration of any of its double-bond isomers: **1** (13%); 1-methyl- (44%), 2-methyl- (44%), and 5-methyl- (1%) cyclo-1,3-hexadienes, and 1-methylcyclohexa-1,4-diene (44%).[14]

(14) Staley, S. W. Thermodynamics of Cyclic Dienes, Ph.D. Dissertation, Yale University, New Haven, CT, 1964.

(15) Ekmanis, J. L. Diradicals in Thermal Rearrangements: A) cis- and trans-Dispiro[5.0.5.2]tetradeca-1,8-dienes; B) Methylenecyclobutane. Ph.D. Dissertation, Harvard University, Cambridge, MA, 1976; *Diss. Abstr. Intern. B* **1976**, *37*, 224B (Order No. 76-14,401).

(16) There are many examples where thermodynamics for dimerization is favorable, among them the spectacular protoanemonin−anemonin system: Moriarty, R. M.; Romain, C. R.; Karle, I. L.; Karle, J. *J. Am. Chem. Soc.* **1965**, *87*, 3251−3252.

(17) (a) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499−2526. (b) Roth, W. R.; Staemmler, V.; Neumann, M.; Schmuck, C. *Liebigs Ann.* **1995**, 1061−1118.

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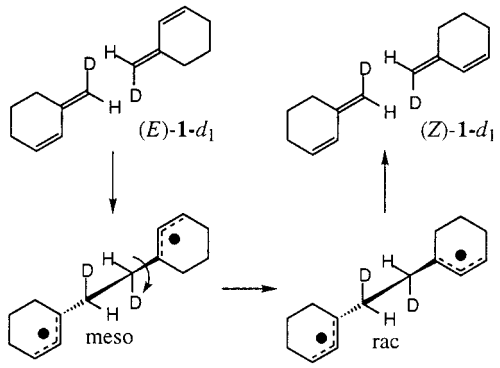
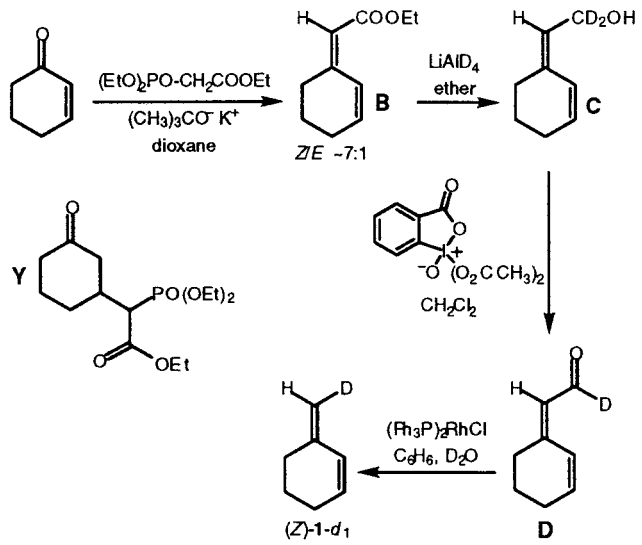


Figure 3. Second-order mechanism for cis,trans isomerization of (*E*)-**1**-*d* to (*Z*)-**1**-*d* is illustrated.

Scheme 1



Despite this failure, a tetramethylene diradical, possibly formed transiently, might be expected to reveal itself through internal rotations prior to reversion (Figure 3). The search for such a second-order, thermally induced stereomutation was undertaken in stereospecifically labeled 3-methylenecyclohexene-*d* [(*Z*)- and (*E*)-**1**-*d*]. No synthetic procedure having been reported for this type, the sequence shown in Scheme 1 was developed. Although several products resulting from Michael addition were formed instead of the desired compound **B** in a Wittig−Horner reaction of cyclohexen-3-one and triethylphosphonoacetate,[19] a good yield of **B** resulted from the use of freshly sublimed potassium *tert*-butoxide and scrupulously dried dioxane.[20] Interestingly, when cursorily dried dioxane, or sodium hydride in tetrahydrofuran, was employed, a high yield of compound **Y** resulted![21] Although the favorable stereochemistry introduced in the first step was not compromised in the unexceptional second step, in the third, oxidation of the hydroxymethyl group by MnO_2[22] led to a useless 1:1 mixture of (*Z*)- and (*E*)-aldehyde. A possibly more felicitous procedure[23] was not explored when it was found that the transformation could be accomplished satisfactorily by using the reagent of Dess and Martin.[24] In the ultimate decarbonmonoxylation by means of chlorotris(triphenylphosphine)rhodium,[25] loss of deuterium was avoided by the addition of a small amount of deuterium oxide, while loss of stereochemistry was mitigated by minimal exposure to the conditions of the reaction. The final product consisted mainly (85%) of (*Z*)-3-methylenecyclohexene-*d* and, to a lesser extent (15%), of the (*E*) isomer. Heating an approximately 10% solution of this mixture in benzene-d_6 (degassed and sealed under vacuum) at 110.5 °C for 117 h led to the recovery only of unchanged material.[26]

In a final effort to effect thermal dimerization, high pressure was applied in the expectation of shifting the equilibrium thermodynamically toward the dimers (vide infra) and accelerating the rate of dimerization, thereby lowering the temperature required for reaction and decreasing the magnitude of the unfavorable $T\Delta S$ term. At 7.5−8.0 kbar and 25−60 °C, dimerization did indeed occur, but only to the extent of ∼1%. Of four compounds observed by capillary GLC, but not isolated, two had the same retention times as *anti*-**2** and *syn*-**2** (vide infra), while the other two, of longer retention times, were not among the minor photochemical products of irradiation of **1**. Lacking a peak at $m/z = 94$ (**1**), and having their major peak at $m/z = 173$, they appeared not to be products of [2 + 2] cycloaddition.

Where thermal dimerization had failed, irradiation of **1** in the presence of the triplet sensitizer, benzophenone,[27] afforded a mixture of *anti*-**2** and *syn*-**2**, contaminated by ∼10% of otherwise unidentified, isomeric impurities of $m/z = 188$. Quantitative analysis was effected by capillary GLC, while preparative separation was accomplished with freshly prepared columns of silver tetrafluoroborate of limited lifespan. Attempts to exploit a possibly greater complexing power of the syn isomer with silver tetrachloroaluminate in benzene achieved little.

Several of the possible structures for the dimers are eliminated by finding that hydrogenation of *anti*-**2** or *syn*-**2** gives a tetrahydro derivative, shown by direct comparison not to be identical to dispiro[5.1.5.1]tetradecane.[28,29] Definitive constitutional assignments are based on ^{1}H and ^{13}C NMR, H−H and C−H correlation spectra, and INADEQUATE measurements.[30] The presence of only seven ^{13}C resonances excludes all but symmetrical structures. Configurational assignments are based on the nuclear Overhauser effect (NOE). Examination of molecular mechanical models (Figure 4) reveals close approaches of ∼2.5 Å in both isomers by double bond hydrons, H-1 and H-2, and H-8 and H-9. Likewise, in both isomers, similarly close approaches are seen for H-1 and H-8 and the respective syn hydrons H-13 and H-14. Distinction between the two configurations rests on an additional close approach between H-1 and *endo*-H-12, and H-8 and *endo*-H-5 in the model of *anti*-**2**, which is not seen in *syn*-**2**. This additional NOE is observed on saturation of H-1 and H-8 ($\delta = 5.79$ ppm) in the isomer of shorter gas chromatographic retention time, to which

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(26) Dimerization under high pressure was not examined owing to very low yields. The stereochemical potential inherent in the photodimers has not been pursued (Figures SI-1 and SI-2).
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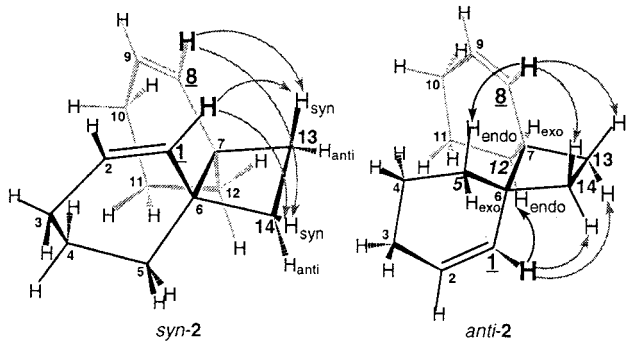

Figure 4. Three-dimensional, molecular-mechanical-generated models of lowest energy conformations of *syn*-**2** (left) and *anti*-**2** (right). Close NOE-active approaches (~2.5 Å; vinyl interactions omitted) of the hydrons at C-1 and C-8 to syn hydrons at C-13 and C-14, respectively, are shown by gray arrows in the cyclobutane ring of both isomers. Additional close approaches (black arrows) of H-1 and H-8 to *endo*-H-12 and *endo*-H-5, respectively, in *anti*-**2,** which are lacking in *syn*-**2**, are also indicated.

Table 1. Specific Rate Constants and Activation Parameters Calculated from the Data in Table S1 for the Stereochemical Interconversions (k_{as} and k_{sa}) and Cycloreversions (k_{am} *and* k_{sm}) of *anti*-**2**-Dispiro[5.0.5.2]tetradeca-1,8-dienes (Figure 1)

T, °C	k_{as}[a]	k_{sa}[a]	k_{am}[a]	k_{sm}[a]
72.1	0.49	0.27	0.70	1.57
72.1[b]	0.44	0.70	0.83	0.93
81.1	1.72		2.27	7.00
92.3	5.90	5.15	9.71	18.3
98.5	11.7	29.7	26.0	16.9
110.9	47.2	73.0	96.4	130
118.2	109	188	208	277

	anti-**2**→*syn*-**2**	*syn*-**2**→*anti*-**2**	*anti*-**2**→**1**	*syn*-**2**→**1**
E_a[b]	31.1 ± 0.4	38.3 ± 3.1	33.5 ± 0.6	28.7 ± 2.7
log A	13.36 ± 0.26	17.7 ± 1.8	15.07 ± 0.37	12.4 ± 1.6
$\Delta H^{\ddagger}$[c−e]	30.3 ± 0.9	37.6 ± 7.2	32.8 ± 1.3	27.9 ± 5.8
$\Delta S^{\ddagger}$[c−e]	0.2 ± 1.7	20.2 ± 8.6	+8.0 ± 2.2	−4.4 ± 7.6

[a] In units of 10^{-6} s^{-1}. [b] Starting from 100% *syn*−**2**; all others from 100% *anti*−**2**. [c] E_a and $\Delta H^{\ddagger}$ in kcal mol^{-1}; $\Delta S^{\ddagger}$ in cal mol^{-1} K^{-1}. [d] Calculated at 95.5 °C. [e] 90% confidence level.

the anti configuration is therefore assigned. The product of hydrogenation can be confidently assigned the structure, dispiro-[5.0.5.2]tetradecane.

The kinetics of the conversion of *anti*-**2** to *syn*-**2**, and of cycloreversion of *anti*-**2** to **1**, have been examined in the temperature range 72.1−118.2 °C in mesitylene as solvent. The main body of data, given in Table SI-1 (Supporting Information), is obtained by following a published procedure.[31] Specific rate constants and derived activation parameters have been calculated by a program, kindly supplied by W. R. Roth, on the basis of the four-parameter equation of Figure 1, and are collected in Table 1. The results of an alternative method of calculation, given in Table SI-2, for the reactions of *anti*-**2** are quite comparable, but those from *syn*-**2** are more sharply defined (see Table 6).[31] From the kinetics relating to *syn*-**2** at 72.1 °C, a ratio of rates of 0.65 emerges for stereochemical interconversion of *anti*-**2** to *syn*-**2**, corresponding to a free energy difference favoring *anti*-**2** by −0.3 kcal mol^{-1}. This small value is consistent with heats of formation calculated by MM2ERW:[17a] *anti*-**2**, 27.46 kcal mol^{-1}; *syn*-**2**, 27.56 kcal mol^{-1} (Benson group equivalent values, 25.2 kcal mol^{-1}).[32]

1-Phenyl-3-methylenecyclohexene (**3**) introduces a radical-stabilizing group in conjugation with the butadiene system, like the third double bond in the hexatriene system, 4a-methyl-2,3,4,-4a,5,6-hexahydro-2(3*H*)-methylenenaphthalene (**5**/**6**).[33] A synthesis reported by Reich and Wollowitz leads to a mixture consisting of **3** (72%), 1-phenyl-3-methylcyclohexa-1,3-diene (21%), and 1-methyl-3-phenylcyclohexa-1,3-diene (7%), which is separated only with great difficulty.[34] Alternatively, a Wittig reaction of methylenetriphenylphosphorane with 3-phenylcyclohex-2-enone yields **3** contaminated by less than 5% of the other isomers.

Table 2. Pressure Dependence of Specific Rate Constants and Volumes of Activation for Stereomutation and Cycloreversion to **1** of *anti*-**2** and *syn*-**2** at 100.5 °C in Heptane

p, bar	*anti*-**2**→*syn*-**2**, k_{as}[a]	*syn*-**2**→*anti*-**2**, k_{sa}[a]	*anti*-**2**→**1**, k_{am}[a]	*syn*-**2**→**1**, k_{am}[a]
1[b]	1.46	2.05	2.68	3.86
1[c]	1.41	2.07	2.68	3.63
200	1.23 ± 0.10	2.00 ± 0.12	2.45 ± 0.09	3.00 ± 0.11
400	1.08 ± 0.11	1.90 ± 0.13	2.51 ± 0.10	2.66 ± 0.13
600	1.09 ± 0.06	1.74 ± 0.08	2.13 ± 0.06	2.77 ± 0.08
800	0.93 ± 0.04	1.49 ± 0.04	1.95 ± 0.03	2.39 ± 0.04
1000	0.82 ± 0.06	1.35 ± 0.07	1.82 ± 0.05	2.14 ± 0.07
1500	0.73 ± 0.06	1.15 ± 0.08	1.50 ± 0.06	1.94 ± 0.07
2000	0.59 ± 0.03	0.95 ± 0.04	1.28 ± 0.03	1.68 ± 0.04
4300	0.29 ± 0.06	0.47 ± 0.08	0.30 ± 0.05	0.98 ± 0.07

$\Delta V^{\ddagger}$[d]	$\Delta V^{\ddagger}_{as}$	$\Delta V^{\ddagger}_{sa}$	$\Delta V^{\ddagger}_{am}$	$\Delta V^{\ddagger}_{sm}$
$\Delta V^{\ddagger}$[e]	+13.9 ± 1.5	+14.7 ± 1.1	+11.9 ± 0.9	+11.2 ± 2.0
$\Delta V^{\ddagger}_0$[f]	+15.4 ± 0.5	+14.2 ± 0.4	+13.0 ± 0.4	+14.5 ± 0.7

[a] Rate constants in units of 10^{-5} s^{-1}. [b] Calculated at 100.5 °C from the Arrhenius parameters in Table SI−2. [c] Values by linear extrapolation to 1 bar from the data over the range, 200−2000 bar. [d] Volumes of activation in cm^3 mol^{-1}. [e] Derived from the data, 1−1500 bar, by the linear correlation, $\ln(k)p = a + bp$, $\Delta V^{\ddagger} = -bRT$($R$ = 83.14 cm^3 bar K^{-1} mol^{-1}). [f] Derived from the data, 1−4300 bar, by the nonlinear correlation, $\ln(k)p = a + bp + cp^2$, $\Delta V^{\ddagger}_0 = -bRT$.

Table 3. Specific Rate Constants at 43.6°C of Stereomutation, *anti* → *syn*, and Fragmentation, *anti* → Monomer, in Systems **1**/**2**, **3**/**4**, and **5**/**6**

	anti → *syn*			*anti* → monomer			
system	E_a[a]	log A	$k_{43.6}$ (s^{-1})	E_a[a]	log A	$k_{43.6}$ (s^{-1})	k_{St}/k_{Fr}
1/**2**	31.1	13.36	0.80×10^{-8}	33.5	15.07	0.91×10^{-8}	0.9
3/**4**[b]	[25.3]	[13.56]	2.01×10^{-4}	[27.9]	[14.77]	0.36×10^{-4}	5.7
5/**6**	21.7	13.75	6.00×10^{-2}	24.8	14.47	0.23×10^{-2}	26.2

[a] In kcal mol^{-1}. [b] E_a are calculated by the Arrhenius equation from experimental values of $k_{43.6}$ and a value for log A taken as the average of the experimental values for systems **1**/**2** and **5**/**6**.

Irradiation of **3** leads to the cyclobutane dimers, *anti*-**4** and *syn*-**4**, to which structures are assigned on the basis of their NMR spectra (Figure 2). These dimers are unstable, undergoing cycloreversion to **3** at room temperature, and are difficult to study kinetically. As a consequence, specific rate constants for their stereomutation and fragmentation have been obtained only at a single temperature, 43.6 °C (Table 4, 1 bar). For purposes of comparison, rate constants at 43.6 °C have been calculated for system **5**/**6**[33] and system **1**/**2** from their respective activation parameters. In a reverse procedure, enthalpies of activation for the system **3**/**4** have been estimated by assuming a value for the Arrhenius log A term equal to the mean of the values found experimentally for systems **1**/**2** and **5**/**6** (Table 3).

Volumes of activation derived from the pressure dependence of rates have become an important variable in efforts to

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(33) Doering, W. v. E.; Belfield, K. D.; He, J.-n. *J. Am. Chem. Soc.* **1993**, *115,* 5414−5421.
(34) Reich, H. J.; Wollowitz, S. *J. Am. Chem. Soc.* **1982**, *104,* 7051−7059.

Table 4. Pressure Dependence of Specific Rate Constants and Derived Volumes of Activation for Stereomutation and Cycloreversion to **3** of *anti*-**4** and *syn*-**4** at 43.6 °C in *n*-Heptane

p, bar	*anti*-**4**→*syn*-**4**, k_{as}[a]	*syn*-**4**→*anti*-**4**, k_{sa}[a]	*anti*-**4**→**3**, k_{am}[a]	*syn*-**4**→**3**, k_{sm}[a]
1	20.14 ± 1.35	35.57 ± 2.16	3.55 ± 0.85	6.14 ± 1.57
1000	10.97 ± 0.75	21.12 ± 1.24	2.34 ± 0.46	3.65 ± 0.88
3000	5.07 ± 0.28	11.34 ± 0.52	1.27 ± 0.16	1.96 ± 0.34

	$\Delta V^{\ddagger}_{as}$	$\Delta V^{\ddagger}_{sa}$	$\Delta V^{\ddagger}_{am}$	$\Delta V^{\ddagger}_{sm}$
$\Delta V^{\ddagger}$[b]	+11.8 ± 1.5	+9.8 ± 1.4[c]	+8.9 ± 0.7	+9.8 ± 1.4[d]

[a] Rate constants in units of 10^{-5} s^{-1}. [b] Volumes of activation in cm^3 mol^{-1} derived from the data at 1, 1000, and 3000 bar by the linear correlation, $\ln(k)_p = a + bp$, $\Delta V^{\ddagger} = -bRT$($R$ = 83.14 cm^3 bar K^{-1} mol^{-1}). [c] Weighted mean, 10.8 cm^3 mol^{-1}. [d] Weighted mean, 9.2 cm^3 mol^{-1}.

Table 5. Partial Molar Volumes V (cm^3 mol^{-1}), Temperature Coefficients κ_0 (K^{-1}) (in *n*-Hexane), and van der Waals Volumes V_W (cm^3 mol^{-1}) of **1**, *anti*-**2**, and *syn*-**2**

	1	*anti*-**2**	*syn*-**2**[a]
V(20 °C)	111.7	198.4	200.4
V(100.5 °C)[b]	121.3	204.2	205.2
κ_0	10.650	3.607	2.996
V_W[c]	66.4	126.6	126.6

[a] V(*syn*-**2**) determined on a mixture of *syn*-**2** (90.2%) and *anti*-**2** (9.8%). [b] Calculated by the equation, $V(100.5\ °C) = V(20\ °C) \times (1 + 80.5\kappa_0)$. [c] Calculated van der Waals volumes.[56]

distinguish between one-step and two-step processes competing within the same system.[35] Although the ad libitum system, butadiene/1,2-divinylcyclobutanes, serves as an excellent example,[36] establishment of the pressure dependence of cycloreversion of *trans*-1,2-divinylcyclobutane to butadiene is subject to a large experimental uncertainty.[37] A more informative example exists in the obligatorily cisoid cyclohexa-1,3-diene system, despite the added complexity of an intramolecular reaction of the "ene" type.[38]

Volumes of activation of systems **1**/**2** and **3**/**4** have been determined from the pressure dependence of the rates of stereomutation and cycloreversion by a previously described procedure.[39] Results are presented in Tables 2 (**1**/**2**) and 4 (**3**/**4**). Furthermore, the temperature-dependent partial molar volumes of **1**, *anti*-**2**, and *syn*-**2** (Table 5) have been determined from measurements of density in the temperature range 20−70 °C (Table SI-3). From these data, volumes of activation of the experimentally not directly observable [2 + 2] cyclodimerization of **1** to *anti*-**2** and *syn*-**2**, respectively, can be calculated. The resulting complete volume profile for the system **1**/**2** is presented in Figure 5.

The effect of pressure on the equilibrium constant for dimerization can be estimated in the following way. From the activation parameters for cycloreversion of *anti*-**2** in Table SI-2 [$\log k_1 = 14.41 - 32400/(RT \ln 10)$], and two sets of parameters available for the dimerization of butadiene as an approximation to what might have been expected of the dimerization of **1** [$\log k_3 = 6.95(8.14) - 27800/(RT \ln 10)$], estimates of $K = [\textit{anti}\text{-}\mathbf{2}]/[\mathbf{1}]^2$ at 293 and 373 K can be made: $9.6(150) \times 10^{-5}$ and $1.8(27) \times 10^{-5}$, respectively. The effect of increasing the pressure to 7000 bar can be estimated from the molar volume of reaction to be a factor of ∼2000 at 293 K. This analysis is consistent with the appearance of only a small amount of dimer under high pressure.

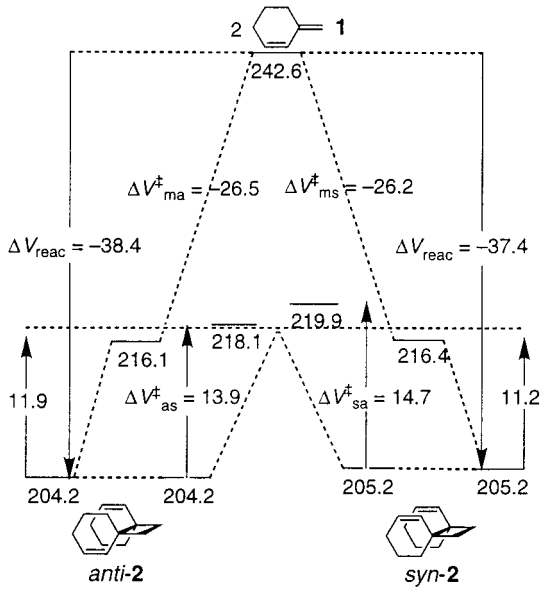

Figure 5. Volume profile for cycloreversion of *anti*-**2** and *syn*-**2** to two **1** (k_{am} and k_{sm}, respectively), and stereomutation of *anti*-**2** and *syn*-**2** (k_{as} and k_{sa}, respectively) in cubic centimeters per mole (see Figure 1).

The difference between the volumes of activation for interconversion of *anti*-**2** and *syn*-**2** ($\Delta\Delta V^{\ddagger} = 0.8$ cm^3 mol^{-1}) agrees well with the corresponding volume of reaction ($\Delta V = 1.0$ cm^3 mol^{-1}), calculated from the partial molar volumes of *anti*-**2** and *syn*-**2** at 100.5 °C (temperature of reaction, Table 5). From the volume profile of the [2 + 2] cycloreversion (Figure 5), activation volumes of the experimentally not observable [2 + 2] cyclodimerization of **1** leading to *anti*- and *syn*-**2**, respectively, can be calculated to be $\Delta V^{\ddagger}$(*anti*-**2**→**1**) = −26.5 cm^3 mol^{-1} and $\Delta V^{\ddagger}$(*syn*-**2**→**1**) = −26.2 cm^3 mol^{-1}. These values are comparable to those determined for the [2 + 2] cyclodimerizations of chloroprene (23 °C, $\Delta V^{\ddagger} = -22$ cm^3 mol^{-1}),[40] 1,3-cyclohexadiene (70.5 °C, $\Delta V^{\ddagger} = -22$ and ‡ −18 cm^3 mol^{-1}) for the formation of the *syn*- and *anti*-[2 + 2] cyclodimers, respectively),[38] and 1,3-butadiene (119.8 °C, $\Delta V^{\ddagger} = -20.9$ cm^3 mol^{-1}).[36]

Activation volumes for cycloreversion and stereomutation in systems **1**/**2** and **3**/**4** ($\Delta V^{\ddagger}$ = 8.9−14.7 cm^3 mol^{-1}) are significantly larger than those determined for stereomutation and cycloreversion of *trans*-1,2-divinylcyclobutane ($\Delta V^{\ddagger} = +4$ to +5 cm^3 mol^{-1})[37] and the reaction volume of the hypothetical isomerization of cyclobutane to butene-1 (ΔV = +6.6 cm^3 mol^{-1}).[41] This difference can be explained by a volume-decreasing, steric interaction of the substituents at the cyclobutane ring of **2** and **4** that is released during ring-opening. The decrease in volume caused by the steric interaction in cis-1,2-disubstituted cyclobutane derivatives can be estimated from the difference between the partial molar volumes of *cis*- and *trans*-1,2-divinylcyclobutane to be $\Delta V = 134.4 - 140.6 = -6.2$ cm^3 mol^{-1}. This value agrees with the cis correction term of −3 cm^3 mol^{-1} used by Exner for the calculation of the molar volumes of cis-1,2-disubstituted alicyclic compounds by volume

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(41) Diedrich, M. K.; Klärner, F.-G. *J. Am. Chem. Soc.* **1998**, *120*, 6212−6218.

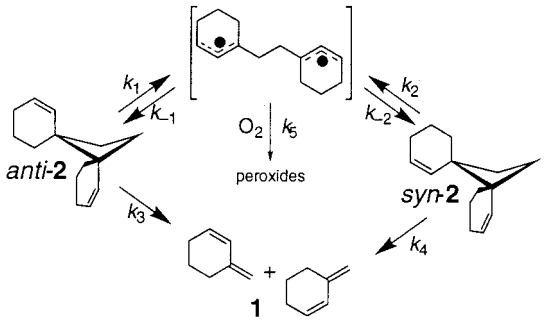

Figure 6. Kinetic scheme for oxygen-trapping in supercritical carbon dioxide of a diradical intermediate in the stereomutation and fragmentation of system **1/2**.

Table 6. Arrhenius Activation Parameters from Oxygen-Trapping Experiments of Roth and Neumann in Supercritical Carbon Dioxide Based on Model in Figure 6 for the Configurational Interconversion and Cycloreversion (k_3 and k_4) of Dispiro[5.0.5.2]tetradeca-1,8-dienes, *anti*-**2** (k_1, k_{-1}) and *syn*-**2** (k_2, k_{-2})

reaction[a]	E_a[b]	log A
k_1	30.3 [30.6][c]	13.26 [13.08]
k_{-1}	2.7	11.55
k_2	29.1 [30.7]	12.89 [13.31]
k_{-2}	2.7	11.64
k_3	32.4 [32.4]	12.89 [14.41]
k_4	31.1 [32.5]	12.89 [14.62]

[a] No confidence limits were reported. [b] In kcal mol^{-1}. [c] The related results of Ekmanis (Table SI-2) are repeated in brackets for convenience in comparison.

increments.[42] No such difference is to be expected between the molar volumes of *anti*-**2** and *syn*-**2**, both of which are 1,1,2,2-tetrasubstituted cyclobutanes.

A powerful, ground-breaking method for trapping intermediate diradicals by oxygen in supercritical carbon dioxide has been introduced by Wolfgang Roth.[43] In many of its applications, this method has led to the *quantitative* establishment of the depth of the enthalpic well into which intermediate diradicals fall. In the development of the method, system **1/2** was one of two selected to demonstrate its validity. These unpublished experimental results are summarized here. Details of the construction and operation of the apparatus are available in the Ph.D. dissertation of Martin Neumann,[18] as are tables of concentrations of **1**, *anti*-**2**, *syn*-**2**, and material lost to peroxide formation, in experiments ranging in temperature from 89.3 to 146.7 °C, and in partial pressures of oxygen from 0 to 83 bar. Although details of the calculation are not given, the authors have developed a program that, using all data simultaneously, generates a best fit of Arrhenius activation parameters by minimizing deviations between calculated and experimental concentrations.[44] The program is applied to the kinetic model in Figure 6, which includes irreversible reaction of an hypothetical diradical intermediate with oxygen on every collision. The absence of evidence for a direct reaction of oxygen with **1** justifies omission of such a step from kinetic models. Activation parameters at atmospheric pressure in the absence of oxygen reported in Table 6 are in satisfactory agreement with those of this work (Table SI-2). They reveal an oxygen-sensitive intermediate stabilized by −2.7 kcal mol^{-1} relative to the transition region for the thermal interconversion of *anti*-**2** and *syn*-**2**. That this oxygen-trapped intermediate be one or the other, or both, of the two conformations of the intermediary diradical (Figures 1 and 6) seems eminently reasonable.

Discussion

Radical-Stabilizing Perturbations. Predicting the effect of perturbations on the rates of not-obviously-concerted thermal rearrangements has a long history of success. Rate determined by generation of diradical intermediates being the basic mechanistic assumption, *enthalpie*s of stabilization of carbon free radicals evaluated independently are merely added to the experimental enthalpy of activation of the unsubstituted paradigm. In a particularly impressive example, Baldwin has found excellent correlation between radical-stabilizing power in *free energy* of a large number of groups and their effect on rates of enantiomerization of trans-1,2-disubstituted cyclopropanes.[45] The fact that enthalpy alone, and enthalpy and entropy together, work equally well indicates that differences in the influence of these perturbations on entropy are minor. In passing, we note the contrast between *not-obviously-concerted* and *concerted* thermal rearrangements. In the latter, prediction of enthalpies of activation has been the frustrating challenge, while prediction of stereochemical preferences among exit channels, thanks to Woodward and Hoffmann, is a surety. In the former it has been the reverse.

The present results from a small series of 1,2-disubstituted cyclobutanes are no exception. System **1**/**2** is the first of three members of a conjugated series, comprising a diene, a triene (**5**/**6**),[33] and a tetraene (**7**/**8**)[46] (Figure 2), designed to evaluate the validity of transferring to cyclobutanes the stabilization enthalpies of polyenyl radicals that had been determined independently by cis−trans geometrical isomerization about the carbon−carbon double bond.[47] An example from the literature is 1,2-divinylcyclobutane. Its enthalpy of activation for cycloreversion is predicted to be lower than that of cyclobutane ($\Delta H^{\ddagger}$ = 61.8 kcal mol^{-1})[48] by twice the stabilization energy of an allyl radical (−13.5 kcal mol^{-1}). The resulting prediction of 34.8 kcal mol^{-1} agrees well with values of 34.0 and 35.7 kcal mol^{-1} reported by Hammond and DeBoer.[27] The experimental value for the more highly substitured but related system **1**/**2** is 32.8 kcal mol^{-1}. The additional small lowering is reasonably ascribed to a rate-enhancing release of the steric repulsion between the two cyclohexenyl rings. In system **3/4**, the vinyl groups in system **1**/**2** have been replaced by the more strongly stabilizing cinnamyl group (stabilization energy, −15.7 kcal mol^{-1}).[37] The predicted enthalpy of activation of 30.4 kcal mol^{-1} compares with the estimated experimental value of 27.0 kcal mol^{-1} (vide supra). The discrepancy is again ascribed to the steric factor. For system **5**/**6** of the 1,2-dibutadienyl type, the stabilization energy advanced for the pentadienyl radical (−16.9 kcal mol^{-1}) leads to an estimated enthalpy of activation of 28.0 kcal mol^{-1} versus the experimental value, 24.0 kcal mol^{-1}.[33] But for a reasonably constant steric correction of ∼3 ± 1 kcal mol^{-1}, the transferability of enthalpies of radical stabilization obtained from thermal cis−trans geometrical isomerization to

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(43) Professor Roth's unfortunate death (October 29, 1997) has prevented him from taking part in this publication.

(44) Privately communicated by Professor W. R. Roth.

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(46) Doering, W. v. E.; He, J.-n.; Shao, L.-m., submitted to *J. Am. Chem. Soc*.

(47) Doering, W. v. E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288−4297. Doering, W. v. E.; Sarma, K. *J. Am. Chem. Soc*. **1992**, *114*, 6037−6043.

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these cyclobutanes is validated. Incidentally, the diradical hypothesis at the base of the prediction also receives support thereby.

The findings that volumes of activation of the syn−anti interconversion of **2** (and **4**) and the [2 + 2] cycloreversion of *syn*- and *anti*-**2** (and *syn*- and *anti*-**4**) are all positive [system **1/2**, $+14.4 \pm 1.3$ and $+11.7 \pm 1.3$ cm^3 mol^{-1}; system **3/4**, $+10.8 \pm 1.5$ and $+9.2 \pm 1.0$ cm^3 mol^{-1}, respectively (mean of values in Tables 2 and 4)], and that each set of data is almost of equal size, provide good evidence that the cyclobutane ring-opening of **2** and **4** leading to the respective diradicals is the rate-determining step of each reaction.

Product Ratios from Diradical Intermediates. The second part of the discussion addresses long-standing difficulties attending attempts to identify factors that may be generally useful for predicting distribution among competing products in not-obviously-concerted thermal rearrangements of small cyclic hydrocarbons and their derivatives. The extraordinarily thorough theoretical investigation of the archetypes, cyclopropane and, of more direct relevance here, cyclobutane, recently published by Doubleday et al.,[1] sharply points to entropy as the product-controlling factor to which our attention should be directed. Their conclusion, largely supported by more recent calculational efforts,[4,49] emphasizes two distinct phases in the thermal behavior of cyclobutane. The first is the conventional, rate-determining entry into a "diradical" transition region characterized as a relatively "flat", multidimensional, free energy "surface" ("generalized common biradical", "continuous diradical as transition state",[50] "twixtyl" [51]—a region we dub "caldera" for want of a current, short-hand appellation). The second is the product-determining phase in which internal rotations interrelate the various conformations of the tetramethylene diradical and are followed either by reclosures leading to stereomutation or by fragmentations to ethylene (cis and trans from appropriately isotopically labeled cyclobutane). These goings-on in the caldera are all under the control of entropy alone, none requiring further enthalpy of activation in the Arrhenius sense.[52]

Is unsubstituted cyclobutane a valid paradigm for substituted cyclobutanes, or is it unique? If the answer is "Yes", it would be better to focus on factors controlling entropies of activation for exit from the caldera; if "No", both enthalpy and entropy remain the focus. In these terms, we examine the response of the much more highly substituted cyclobutanes of this paper to temperature and pressure.

Were pressure to influence not only entry into the caldera, but exit from it, the volume of activation for fragmentation in systems such as **1/2** and **3/4** might be expected to be significantly *more positive* than that for stereomutation. Fragmentation should require a further increase in volume as the transition region begins to combine the elements of the diradical intermediate with the larger molar volume of the two monomers. Its magnitude, to be sure, might depend on how close the transition region was to the diradical—small but positive, if the path were downhill with no barrier; larger, the more so, the closer the transition region to the two dissociated monomers. Stereomutation, by contrast, should require only internal rotations and reclosure, "two processes" expected to be associated with a negligible change in volume for the internal rotations and a volume contraction for the recyclization of the diradical. The observation that volumes of activation for fragmentation and stereomutation are essentially identical is consistent with the Doubleday conceptual scheme of control by entropy.

A contrasting example is found in the [2 + 2] cycloaddition of 1,1-difluoroallene to (*Z*)-*β*-deuteriostyrene. A substantial increase of stereoselectivity in favor of *cis*-2-deuterio-3-phenyl-1-methylenecyclobutane derivatives is observed upon raising the pressure from 1.8 to 13 kbar. In this case it can be concluded that the activation volume of the ring-closure of the initially formed diradical intermediates leading to the (*Z*)-methylenecyclobutane derivatives is indeed, as expected, more negative than that of bond rotations, a prerequisite for the formation of the corresponding (*E*)-methylenecyclobutane derivatives.[53]

Variation of temperature normally would allow distinction between processes under control by entropy alone and those under control by enthalpy and entropy, or enthalpy alone. Under entropy control, the ratio of stereomutation to fragmentation should be virtually independent of temperature. In both systems **1/2** and **5/6**, enthalpies of activation for fragmentation, however, appear to be 2−3 kcal mol^{-1} higher than those for stereomutation. But we caution that the entropies of activation are in a discouragingly compensating direction ($\Delta \log A \approx 1$), and that the differences in enthalpies of activation are of the same order of magnitude as the experimental uncertainties. Some theoretical support comes from the study of the butadiene/4-vinylcyclohexene system by Li and Houk,[54] who find that the gauche 1,2-bis-allylethane diradical requires an activation energy of only 1.4 kcal mol^{-1} for ring closure (to 4-vinylcyclohexene), but 5.0 kcal mol^{-1} for fragmentation to two molecules of butadiene. Nonetheless, to conclude that our observed temperature dependence argues against exclusive control by entropy is problematic.

We foresee much experimentally painstaking kinetic work before the Doubleday question finds its clarification.

Experimental Section

General. Infrared spectra (IR) were recorded on a Perkin-Elmer model 337 spectrophotometer and are reported in ν (cm^{-1}). Ultraviolet spectra (UV) were recorded on a Perkin-Elmer model 202 or a Unicam model SP spectrophotometer [λ_{max} in nm (log ϵ)]. ^{1}H NMR spectra were measured in $CDCl_3$ (δ, referenced to TMS, 0.0 ppm) or C_6D_6 (referenced to C_6D_5H, 7.15 ppm) on Bruker AM-200, AM-300, AM-400, and AM-500 instruments as noted. Coupling constants, *J*, are given in hertz. ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker AM-300 (75.5 MHz) spectrometer. Mass spectra were recorded on an AEI model MS 9 double-focusing instrument, and on a JEOL JMS-AX505H mass spectrometer coupled to a Hewlett-Packard 5890 Series II gas chromatograph (GC/MS), and are reported as *m*/*z* (% relative to strongest peak, 100). Refractive indices were obtained with a Bausch & Lomb Abbé refractometer. Melting points were taken in open capillaries with a Meltemp apparatus and are uncorrected. Concentrations are given as volume/volume (v/v) for liquids and weight/volume (g/mL) for solids. Distillations were performed on a Piros-Glover spinning band MicroStill (H. S. Martin & Son, Evanston, IL). Reactions were monitored by gas chromatography on a Perkin-Elmer 990 instrument equipped with a DISC integrator. Capillary gas liquid chromatography (GLC) was conducted on a Hewlett-Packard GC model 5890, equipped with an integrator, model 3393A, and a flame ionization detector, using a DB-1 column (J&W Scientific, 1.5 μm film thickness, 30 m × 0.523 mm; He, 3.7 mL/min). Preparative GLC was performed on an Aerograph Fractometer model A-90, and an Aerograph Autoprep model A-700, using the following columns. Stainless steel: (I) 4 m, 10% nitrile silicone (XF 1150); (II) 300 ft × 0.01 in. i.d., open tubular

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(Golay), methyl silicone (OV 101); (III) 50 ft × 0.02 in. i.d., support-coated, open tubular (SCOT), cyanopropylmethyl phenylmethyl silicon (OV 225). Aluminum ($^1/_4$ in. o.d.; 60/80 mesh Chromosorb P): (IV) 1 m, 8% $AgBF_4$ and 10% Carbowax 600; (V) 4 m, 10% Dow Corning 710 silicone oil. HPLC columns: (VI) Nucleosil 100-5 NO_2 Vario Prep ET 250/10 column (Machery-Nagel); (VII) Nucleosil 100 NO_2, 3 m × 1 cm i.d. (Fa. Knauer).

3-Methylenecyclohexene (1). 3-Acetoxymethylcyclohexene (**A**) was prepared by a slight modification of the procedure of Blomquist et al.[10] Freshly distilled cyclohexene (1250 g, 15.22 mol) was heated at 185 °C in an autoclave with paraformaldehyde (375 g, 12.5 mol), glacial acetic acid (450 g, 7.5 mol), and acetic anhydride (375 g, 3.7 mol) under vigorous stirring, yielding a dark-brown residue after workup. Distillation in vacuo (water aspirator) yielded four fractions in amounts of 2.3, 203.5, 65.6, and 7.2 g, bp 25−79, 78−83, 99−102, 142 °C, and n_D^{25} 1.4532, 1.4578, 1.4593, and 1.4676, respectively (lit.[10] bp 104−107 °C/35 mmHg; n_D^{25} 1.4564−1.4575). Analysis by GLC (column I, 143 °C, He 15 lb) showed the four fractions to contain 60%, 92%, >99%, and 27%, respectively, of **A** (t_r = 11 min): IR (CCl_4) 3005, 2923, 2872, 2846, 2821, 1742 (vs), 1462, 1444, 1430, 1380, 1362, 1281, 1263, 1230, 1083, 1049, 1032, 976, 891, 860, 719, 699, 680; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (d, 1H, J = 11), 5.56 (d, 1H, J = 11), 3.93 (d, 2H, J = 7), 2.40 (m, 1H), 2.04 (s, 3H), 2.0−1.2 (m, 6H).

A sample of **A** (156.3 g; fractions 2 and 3 above; 94.5% purity) was pyrolyzed at 570−580 °C in a quartz tube packed with quartz chips.[11] Distillation of the crude product yielded 42.3 g of **1** (94% of purity), along with 39 g of recovered starting material. Redistillation yielded 24.5 g of 3-methylenecyclohexene (18% of theoretical yield, 99.6% purity): IR (CCl_4) 3075, 3024, 2971, 2936, 2930, 2891, 2876, 2864, 2830, 1771, 1638, 2599, 1457, 1437, 1418, 1384, 1342, 1246, 1213, 1138, 1137, 1056, 1049, 990, 978, 962, 908, 884 (exocyclic methylene), 861, 706, 666, 562; ^{1}H NMR (400 MHz, C_6D_6) δ 6.16 (dt, 1H, J = 10.0, 2.0, H-2), 5.68 (dt, 1H, J = 10.0, 4.1, H-1), 4.80 (s, 1H, *E*- ═CH), 4.74 (s, 1H, *Z*- ═CH), 2.22 (bt, 2H, J = 6.3, H-4), 1.86 (m, 2H, H-6), 1.52 (quint, 2 H, J = 6.1, H-5); UV (6.92 mg/L, EtOH), 232 (4.272); GC/MS (70 eV) *m*/*z* 94 (M^+, 41), 95 (4), 93 (14), 92 (2.4), 91 (19.8), 79 (100), 77 (36).

3-[(*Z*)-Methylene]cyclohex-1-ene-*d* (1-(*Z*)-*d*). Ethyl (*Z*)- and (*E*)-2-(3-cyclohex-1-enylidene)acetate [(*Z*)-**B** and (*E*)-**B** of Scheme 1] were prepared according to the method of Bensel et al.[20] To a stirred solution of freshly sublimed potassium *tert*-butoxide (28.1 g, 250 mmol) in 600 mL of 1,4-dioxane (throughout, freshly distilled from lithium aluminum hydride ($LiAlH_4$) and degassed) was added a solution of 65.5 g of ethyl diethylphosphonoacetate (Fluka) in 220 mL of dioxane via cannula under argon with stirring over 2.7 h at room temperature. After an additional 40 min of stirring, 20.0 g of 2-cyclohexenone (Aldrich) in 250 mL of dioxane was added via cannula over a 45-min period. After having been stirred for 6.5 h at room temperature and 6 h under reflux, the dark orange reaction mixture was concentrated in vacuo, treated with crushed ice and water, and extracted with ether (3×). The combined ethereal extracts were washed with saturated NaCl (3×), dried over MgSO4, and concentrated in vacuo to a yellow residue, which yielded 9.16 g (27%) of a clear, colorless liquid on distillation: bp 50−55 °C (0.5 mmHg) [lit.[20] bp 95 °C (8 mmHg)]. Analysis by capillary GLC (column DB-1) revealed a ratio (*Z*)/(*E*) = 7.9/1.0. Purification by flash column chromatography (silica gel; 25:1 hexane/ethyl acetate) provided enriched material, (*Z*)/(*E*) = (12−17)/1.0. Data for (*Z*)-**B**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dad, 1H, J = 10.4, 2.2, 0.9, H-2), 6.13 (dad, 1H, J = 10.3, 4.2, 1.6, H-1), 5.38 (s, 1H, C*H*CO_2Et), 4.06 (q, 2H, J = 7.1, OCH_2), 2.30 (td, 2H, J = 6.4, 1.5, H-4), 2.13 (m, 2H, H-6), 1.69 (quintet, 2H, J = 5.9, H-5), 1.18 (t, 3H, J = 7.2, CH_3); ^{13}C NMR (300 MHz, $CDCl_3$, proton decoupled) δ 165.7 (C═O), 151.7 (C-3), 137.4 (C-1), 124.9 (C-2), 112.7 (═*C*HCO_2Et), 58.9 (OCH_2), 32.1 (C-4), 25.7 (C-6), 22.3 (C-5), 13.9 (CH_3). Data for (*E*)-**B**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (brdt, 1H, J = 8.5, H-1), 5.57 (brm, 1H, H-2), 5.47 (s, 1H, C*H*CO_2Et), 4.06 (q, 2H, J = 7.1, OCH_2), 2.98 (brm, 2H, H-4), 2.88 (brm, 2H, H-6), 1.69 (quintet, 2H, J = 5.9, H-5), 1.18 (t, 3H, J = 7.2, CH_3).

(*Z*)- and (*E*)-2-(3-cyclohex-1-enylidene)ethanol-1,1-d_2 (C) was prepared from 10.0 g of **B** and 1.56 g of $LiAlD_4$ (Aldrich, 98% D) in ether (0 °C to 25 °C, 19 h). Purification by column chromatography (elution successively with 25:1, 10:1, and 3:1 hexane/ethyl acetate) afforded 5.74 g (76%) of a pale yellow liquid, analysis by capillary GLC showing a ratio (*Z*)/(*E*) = 8/1. Data for (*Z*)-**C**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (dd, 1H, J = 10.0, 0.7, H-2), 5.89 (dtd, 1H, J = 10.1, 4.1, 1.6, H-1), 5.30 (s, 1H, ═C*H*CD_2H), 4.24 (d, 2H, J = 7.2, CH_2OH), 2.99 (s, 1H, OH), 2.30 (td, 2H, J = 6.2, 1.5, H-4), 2.14 (m, 2H, H-6), 1.70 (p, 2H, J = 6.2, H-5). Data for (*E*)-**C**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (dt, 1H, J = 9.9, 1.9, H-2), 5.80 (m, 1H, H-1), 5.39 (s, 1H, ═C*H*CD_2OH), 4.28 (d, 2H, J = 7.2, CH_2OH), 2.99 (s, 1H, OH), 2.35 (m, 2H, H-4), 2.14 (m, 2H, H-6), 1.70 (p, 2H, J = 6.2, H-5).

(*Z*)- and (*E*)-2-(1-Cyclohex-2-enylidene)acetaldehyde-1-*d* (D). To 26.7 g (63 mmol) of periodinane[24] in 700 mL of CH_2Cl_2 was added a solution of 4.05 g (32.1 mmol) of **C** at 25 °C. After being stirred for 55 min and cooled to 0 °C, the mixture was treated with 300 mL of 0.01% aqueous KOH. The CH_2Cl_2 layer was separated, and the aqueous layer was extracted with ether (3×). The combined organic layers were washed with 0.01% aqueous KOH (3×), water, and saturated aqueous NaCl and dried over $MgSO_4$. Concentration in vacuo gave a yellow liquid with a cinnamon-like odor, purification of which by column chromatography (elution with 25:1 hexane/ethyl acetate) afforded 2.11 g (53.4%) of **D**. Data for (*Z*)-**D**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, 1H, J = 10.1, H-2), 6.37 (dtd, 1H, J = 10.1, 4.2, 1.5, H-1), 5.69 (s, 1H, ═C*H*CDO), 2.50 (td, 2H, J = 6.4, 1.3, H-4), 2.29 (m, 2H, H-6), 1.83 (p, 2H, J = 6.3, H-5). Data for (*E*)-**D**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (dt, H, J = 9.8, 1.8, H-1), 5.76 (s, 1H, ═C*H*CDO), 5.36 (m, 1H, H-2), 2.90 (td, 2H, J = 6.4, 1.8, H-4), 2.29 (m, 2H, H-6), 2.04 (m, 2H, H-5).

Chlorotris(triphenylphosphine)rhodium (925 mg, 1.0 mmol, Strem), 2 g of C_6D_6, and 240 mg of D_2O (12.0 mmol)[25] were heated to reflux. A solution of 135 mg of **D** (1.1 mmol) in 1 g of C_6D_6 was then added via syringe to the stirred, brick red suspension. After being stirred at reflux for 15 min and cooled, the reaction mixture was treated with 1.5 mL of absolute ethanol and 2 mL of pentane. Passage through a short column of silica gel (elution with pentane) gave a dark red solution, which was washed with water (2×) and saturated aqueous NaCl (2×) and dried over K_2CO_3. Fractional distillation in vacuo gave a colorless solution containing C_6D_6 and mainly (*Z*)-**1**-*d* (identified by capillary GLC, GC/MS, and ^{1}H and ^{13}C NMR). GC/MS analysis (electron impact, 70 eV) confirmed the predominant formation of 3-(methylene-*d*)cyclohexene (**1**-*d*): *m*/*z* 95 (M^+, 46), 96 (6), 94 (13), 93 (6), 92 (22), 80 (100), 79 (68), 78 (43). ^{1}H NMR indicated a ratio **1**-(*Z*)-*d*/**1**-(*E*)-*d* of 5.5/1 (determined by cutting and weighing printouts of the ═CHD absorbances at 4.74 [(*Z*) ═CHD] and 4.80 [(*E*) ═CHD]: ^{1}H NMR (400 MHz, C_6D_6) δ 6.18 (dt, 1H, J = 9.9, 2.1, H-2), 5.68 (dtd, 1H, J = 10.0, 4.1, 1.6, H-1), 4.74 (s, 1H, ═CHD), 2.22 (td, 2H, J = 6.3, 1.7, H-4), 1.85 (m, 2H, H-6), 1.52 (p, 2H, J = 6.2, H-5).

Thermal Dimerization of 3-Methylenecyclohexene (1). Sealed tubes containing 51 mg of diphenylamine and 291 mg of **1** were heated at temperatures ranging between 116 and 150 °C for 4 h. Analysis by GLC on column II (50 °C, 1.8 mL He/min) showed no dimer and almost complete recovery of **1**.

When a solution of 48 mg of **1** in 0.5 mL of toluene-d_8 (dried over $LiAlH_4$) was heated at 8 kbar for 48 h at 100 °C, polymer was formed in large amount but could be removed by passing through a short silica gel column prior to analysis by capillary GLC (Carbowax 20M-K, 90 °C). No evidence of dimerization could be detected. Similarly, a solution of 0.5 g of **1** in 10 mL of toluene, when maintained at 8.5 kbar for 65 h at ca. 10 °C, showed no significant change. A more concentrated solution of **1** [260 mg in 0.6 mL of toluene containing a few crystals of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl)sulfide (BHMPS)] maintained at 60 °C for 48 h revealed four products in total yield <1% and relative amounts 19.6, 20.2, 47.5, and 12.7%. *anti*-**2** and *syn*-**2** were identified by GLC: t_r = 15.63 and 16.93 min, GC−MS *m*/*z* (relative intensity) 188 (3), 160 (3), 150 (3), 117 (4), 94 (45), 79 (100), 39 (29). Two unidentified products had the following properties: t_R = 19.15 min, GC−MS *m*/*z* (relative intensity) 188 (100), 173 (98), 160 (39), 145 (23), 131 (93), 117 (48), 91 (63), 79 (56); and t_R = 21.30 min, GC−MS *m*/*z* (relative intensity) 188 (87), 173 (80), 160 (35), 145 (77), 131 (82), 117 (41), 95 (100), 79 (61). An identical solution maintained

at 25 °C and 7.5 kbar for 192 h yielded only *anti*-**2** and *syn*-**2** in equal amounts in a yield <1%.

***anti*- and *syn*-Dispiro[5.0.5.2]tetradeca-1,8-dienes (*anti*-2 and *syn*-2).** A solution of 5.61 g (6 mL, 59.7 mmol) of **1** (99.8% of purity) and 0.44 g (2.4 mmol) of benzophenone was partitioned among eight ampules (7 mm o.d. × 150 mm). The ampules were degassed, sealed under vacuum, and irradiated at 25−35 °C for 12 days in a "merry-go-round" apparatus with a 450-W, high-pressure Hanovia lamp equipped with a 2800-Å cutoff filter. The mass spectra of the combined samples recorded at 14 and 70 eV showed main peaks at *m*/*z* 188 (parent), 160, and 94. Evaporative distillation at 60 °C and 0.01 mmHg yielded 2.8 mL of clear, colorless liquid and a very thick, light yellow residue that was not further investigated. Analysis by GLC of a 10% benzene solution of the distillate on column III (80 °C, injector 90 °C, detector 97 °C, He 4 lb, flow rate 5.5 mL/min) showed two peaks of t_r = 70.7 and 78.3 min in a ratio of 58.8 to 41.2, respectively. The dimers were separated by preparative GLC on silver tetrafluoroborate column IV (85 °C, injector 140 °C, detector 165 °C, He 20 lb, flow rate 280 mL/min); t_r(*anti*-**2**) = 18.5 min; t_r(*syn*-**2**) = 38.0 min. The column was operated above 65 °C, the highest temperature generally recommended for silver nitrate columns, but necessary to keep retention times within reasonable limits. At 85 °C, the useful lifetime of column IV was 8−12 h. The separated *anti*-**2** (340 μL) contained <1% *syn*-**2**, while *syn*-**2** (315 μL) contained 3.4% of *anti*-**2**. Additional purification (rechromatography for *syn*-**2**, and molecular distillation for *anti*-**2**) afforded samples of purity 98.1% and 98.7%, respectively. Data for *syn*-**2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dt, 2H, $^3J_{cis}$ = 10.1, $^4J_{H1-H3}$ = 2.1, H-1,8), 5.61 (dt, 2H, $^3J_{cis}$ = 10.1, $^3J_{H2-H3}$ = 3.6, H-2,9), 1.91 (m, 4H, H-3,10), 1.73 (m, 6H, H-13,14, H-5,12$_{exo}$), 1.51 (m, 6H, H-4,-11, H-5,12$_{endo}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3 (C-1,8), 126.0 (C-2,9), 44.7 (C-6,7), 30.5 ($^1J_{HC}$ = 126, C-5,12), 29.9 ($^1J_{HC}$ = 135, C-13,14), 25.5 ($^1J_{HC}$ = 126, C-3,10), 19.9 ($^1J_{HC}$ = 126, C-4,11); IR (CCl_4) 3014, 2955, 2939, 2923, 2909, 2855, 2828, 2649, 1694, 1638, 1448, 1438, 1430, 1392, 1342, 1290, 1267, 1256, 1220, 1192, 1173, 1159, 1137, 1111, 1096, 1060, 1055, 965, 955, 937, 922, 900, 887, 858, 844, 724, 708, 700, 687, 679, 620. Data for *anti*-**2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (dt, 2H, $^3J_{cis}$ = 10.1, $^4J_{H1-H3}$ = 2.0, H-1,8), 5.64 (dt, 2H, $^3J_{cis}$ = 10.1, $^3J_{H2-H3}$ = 3.6, H-2,9), 1.88 (m, 4H, H-3,10), 1.73 (m, 6H, H-13,14, H-5,12$_{exo}$), 1.51 (m, 6H, H-4,11, H-5,12$_{endo}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.2 (C-1,8), 126.8 (C-2,9), 44.6 (C-6,7), 32.1 ($^1J_{HC}$ = 124, C-5,12), 30.5 ($^1J_{HC}$ = 134, C-13,14), 25.3 ($^1J_{HC}$ = 125, C-3,10), 19.9 ($^1J_{HC}$ = 125, C-4,11); IR 3021, 2961, 2937, 2861, 2836, 2655, 1702, 1641, 1455, 1446, 1434, 1397, 1346, 1290, 1259, 1234, 1221, 1172, 1162, 1138, 1055, 1037, 1000, 961, 943, 933, 928, 918, 886, 859, 842, 724, 708, 700, 685, 621.

Dispiro[5.0.5.2]tetradecane. A solution of 91.7 mg of *anti*-**2** and *syn*-**2** (58.8:41.2) in 3 mL of acetic acid was hydrogenated over PtO_2 (10.1 mg in 12 mL of acetic acid) at 23 °C for 30 min, by which time absorption was complete. The reaction mixture was diluted with water (30 mL) and extracted with 25 mL of ether (2×). The combined ether extracts from three runs were washed with 50 mL of 10% Na_2CO_3 (4×) and dried over $MgSO_4$. Removal of the solvent and molecular distillation of the orange residue gave 170 mg (60.4%) of product. Analysis by GLC on column V (167 °C, He 20 lb) revealed three compounds in the ratio 1.4% (t_r = 19.5 min), 5.9% (t_R = 22.5 min), and 92.7% (t_r = 26 min). Preparative GLC on the same column gave dispiro[5.0.5.2]tetradecane (98% of purity): IR (CCl_4) 2914, 2837, 1446, 1289, 1277, 1220, 1186, 1165, 1148, 954, 927, 906, 884, 845, 734; ^{1}H NMR (100 MHz, CCl_4) δ 1.8−0.8 (broad multiplet containing a sharp singlet at δ 1.59); MS *m*/*z* (70 eV) 192 [M^+], 164, and 96, inter alia.

Dispiro[5.1.5.1]tetradecane. This compound was prepared by literature procedures with one modification.[28,29] Reduction of 14,14-di(ethylmercapto)dispiro[5.1.5.1]tetradecan-7-one with active Raney nickel (920 g, W. R. Grace & Co.) proceeded to dispiro[5.1.5.1]-tetradecan-7-ol, which then had to be oxidized to the corresponding ketone. The alcohol was obtained as colorless crystals on recrystallization from acetonitrile at −10 °C: mp 75−78 °C; IR (CCl_4) 3611, 3477, 2916, 2845, 1447, 1436, 1396, 1281, 1254, 1161, 1148, 1138, 1111, 1080, 1055, 1030, 960, 938, 842; ^{1}H NMR (100 MHz, CCl_4) δ 3.42 (d, 1H, *J* = 7), 1.38 (m, 22H, sharp shoulders at 1.26 and 1.07). Oxidation of the alcohol was effected with chromic acid to give crude ketone (96.3%), recrystallization of which from acetonitrile (60 mL) afforded colorless needles of dispiro[5.1.5.1]tetradecane-7-one: mp 82.5−84.5 °C (lit.[28] mp 85−87 °C); IR (CCl_4) 2927, 2849, 1764 (vs), 1448, 1342, 1303, 1286, 1273, 1252, 1226, 1213, 1157, 1150, 1128, 1120, 1084, 1029, 991, 982, 962, 928, 863, 842. The final product of the sequence was recrystallized from acetonitrile and sublimed to yield pure dispiro[5.1.5.1]tetradecane: mp 55.5−56.8 °C (lit.[28] mp 56.5−58.0 °C). Analysis by GLC on column III (190 °C, He 35 lb, flow rate 1.8 mL/min) showed a single peak, t_r = 16.6 min, to be compared with 19.4 min for dispiro[5.0.5.2]tetradecane under identical conditions.

Pressure Dependence of Thermal Reactions of Dispiro[5.0.5.2]-tetradeca-1,8-diene (2). For the kinetic studies, portions of standard solutions of *anti*-**2** and *syn*-**2**, each in >96% of purity, with *n*-$C_{15}H_{32}$ and *n*-$C_{10}H_{22}$ as internal standards and catalytic amounts of BHMPS (to prevent radical-induced polymerization) in anhydrous *n*-hexane were thermolyzed at 100.5 °C at the pressures given in Table 2. For each pressure, 7−11 samples of each standard solution were taken and analyzed by GLC [fused silicon oil BP225, 30 m; temperature program, 50 °C for 4 min, then heating at a rate of 10 °C/min to 100 °C; carrier gas, He; retention times in min, 1.2 (*n*-hexane), 2.1 (**1**), 2.9 (*n*-$C_{10}H_{22}$), 13.2 (*n*-$C_{15}H_{32}$), 16.7 (*anti*-**2**), and 19.7 (*syn*-**2**)]. At each pressure, the specific rate constants (Table 2) were derived from the two sets of product ratios, obtained from thermolysis of *anti*-**2** and *syn*-**2**, by numerical integration by the use of the Runge−Kutta procedure of fourth order and optimization by the Marquardt method.[55]

Measurements of Partial Molar Volumes of 1, *anti*-2, and *syn*-2. For each substance, densities of solutions at six different concentrations were determined (Table SI-2). Measurements were performed in the temperature range 20−70 °C, in 5° steps. For each temperature, the value of Φ_V (partial molar volume of a substance at a given concentration) was calculated according to the equation,

$$\Phi_V = M/d_0 - (1000/c)[(d - d_0)/d_0]$$

where c (mol L^{-1}) is the concentration of the solution, M (g mol^{-1}) the molar mass of the solute, d (g cm^{-3}) the density of the solution, and d_0 (g cm^{-3}) the density of the pure solvent.[56]

The partial molar volume, V, was calculated by linear extrapolation of Φ_V to a concentration c = 0. The κ_0 values in Table 6 were derived from the temperature dependence of the partial molar volume by use of the equation, $V_T = V_0[1 + \kappa_0(T - T_0)]$, where T_0 = 20 °C.[57] van der Waals volumes V_W were calculated by the computer program MOLVOL.[58]

1-Phenyl-3-methylenecyclohexene (3). The procedure of Reich and Wollowitz[34] yielded a mixture of **3** (72%), 1-phenyl-3-methylcyclohexa-1,3-diene (21%), and 1-methyl-3-phenylcyclohexa-1,3-diene (7%), which could be separated only very tediously by high-performance liquid chromatography (HPLC, column VI) owing to the closeness of retention times. ^{1}H NMR spectra on the mixture (200 MHz, $CDCl_3$): 1-phenyl-3-methylcyclohexa-1,3-diene, δ 6.22 (s, 1H, H-2), 5.6 (m, 1H, H-6), 2.43 (s, 3H, CH_3), 2.6−2.1 (m, 4H, H-4,5); 1-methyl-3-phenylcyclohexa-1,3-diene, δ 6.08 (s, 1H, H-2), 5.93 (t, 1H, H-4), 2.43 (s, 3H, CH_3), 2.1−2.6 (m, 4H, H-5,6).

The procedure of Woods and Tucker was a substantial improve-

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ment.[59] 3-Phenylcyclohex-2-enone, the ultimate intermediate, was obtained in 55% of the theoretical yield after crystallization from cyclohexane: mp 64.5−66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.33 (m, 3H), 6.37 (d, 1H, $^4J_{H2-H6} = 1.0$, H-2), 2.70 (dt, 2H, $^4J_{H6-H2} = 1.0$, H-6), 2.42 (t, 2H, $^3J_{H4-H5} = 6.3$, H-4), 2.08 (m, 2H, $^3J_{H5-H4} = 6.3$, $^3J_{H5-H6} = 6.0$, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9 (C-1), 159.8 (C-3), 129.8 (C-2), 128.5, 125.8, 125.1, 37.0 (C-6), 27.8 (C-4), 22.6 (C-5).

To a suspension of 25.0 g of methylytriphenylphosphonium bromide in 600 mL of anhydrous ether at 0 °C was added 30 mL of a 2.5 M solution of butyllithium in *n*-hexane rapidly under argon and with stirring for 1 h. Over a 3-h period, a solution of 10.4 g of the ketone above in 200 mL of anhydrous ether was added dropwise. Addition of 200 mL of water, followed by extraction with ether (3×), gave combined extracts which were dried over $MgSO_4$. Concentration gave an oil, from which 2.8 g (27.5%) of 1-phenyl-3-methylenecyclohexene (**3**) was obtained as a colorless liquid after being passed through a short column of Al_2O_3: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45, 7.32, 7.24 (m, 5H, H_{phenyl}), 6.59 (s, 1H, H-2), 4.90 (d, 2H, H-7), 2.52 (t, 2H, H-6), 2.40 (dt, 2H, H-4), 1.85 (m, 2H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) 143.7 (C-1), 141.2 (C-3), 139.0, 128.5, 127.5, 125.0 (C_{phenyl}), 126.4 (C-2), 111.4 (C-7), 30.1 (C-6), 27.3 (C-4), 23.0 (C-5).

A 45-mg sample of **3** in 150 mL of $LiAlH_4$-dried heptane was transferred to a triethylamine-deactivated poly(tetrafluoroethylene) (PTFE) sack containing a few crystals of BHMPS, placed in a 14-kbar, high-pressure autoclave, and kept at 25 °C and 10.2 kbar for 48 h. Abter being passed through a short column of Al_2O_3 (heptane) to remove colorless polymeric material, the sample showed no recovered **3** and no new products on analysis by HPLC.

2,9-Diphenyldispiro[5.0.5.2]tetradeca-1,8-diene (4). A solution of 700 mg of **3** and 100 mg of benzophenone in 10.0 mL of $LiAlH_4$-dried heptane was freed of oxygen by three pump−freeze cycles and placed under argon in a Pyrex irradiation apparatus that could be cooled by circulating methanol externally cooled to −40 °C. Irradiation with a high-pressure mercury lamp (150 W) for 72 h generated some insoluble polymer, removed by filtration through a short column of Al_2O_3. Analysis of the resulting heptane solution by HPLC on column VII showed two major products, *anti*-**4** (t_R = 18.23 min) and *syn*-**4** (t_R = 21.12 min), in addition to 10 other products in minor amounts. Although unstable at room temperature and above, *anti*-**4** and *syn*-**4** could be separated by semipreparative HPLC (column VI) and stored for weeks at −30 °C. Data for *anti*-**4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 10H, H_{phenyl}), 6.20 (s, 2H, H-1,8), 2.26 (m, 4H, H-3,10), 1.98 (m, 2H, H-5,12$_{exo}$), 1.87 (AA′BB′, 4H, $^2J_{Hanti-13-Hsyn-14} = 7.3$, H-13,14), 1.63 (m, 6H, H-4,11, H-5,12$_{endo}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9 (C-2,9), 136.9 (C_{phenyl}), 131.2 (C-1,8), 128.4, 126.8, 125.4 (C_{phenyl}), 46.2 (C-6,7), 32.1, 31.1, 27.9 (C-13,14, C-5,12, C-3,10), 20.5 (C-4.11). Data for *syn*-**4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (m, 10H, H_{phenyl}), 6.34 (s, 2H, H-1,8), 2.28 (m, 4H, H-3,10), 1.7 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4 (C-2,9), 135.5 (C_{phenyl}), 131.9 (C-1,8), 128.2, 126.6, 125.1 (C_{phenyl}), 44.2 (C-6,7), 30.0, 29.8, 27.6 (C-13,14, C-3,10, C-5,12), 20.1 (C-4,11).

Pressure Dependence of Thermal Reactions of 2,9-Diphenyldispiro-[5.0.5.2]tetradeca-1,8-diene (4). For kinetic studies, standard solutions of *anti*-**4** and *syn*-**4** each in >98% of purity were prepared by separating the appropriate fractions from HPLC column VI above and evaporating to a concentration of ∼1%. Mesitylene was added as a UV-active, internal standard. The solutions were degassed by the pump−freeze method and stored at −30 °C.

For the kinetics at 1 bar, 10-μL portions of the solutions (separate runs each for *anti*-**4** and *syn*-**4**) were heated in a two-necked flask (one neck of which was fitted with a T-tube and bubble counter to allow control of the rate of flow of argon), and maintained at 43.6 ± 0.1 °C. At 15-min intervals, 200-μL samples were removed by syringe through a septum and analyzed on HPLC column VII [50-μL injections; 1.5 mL/min (120 bar) for 5 min; 2.0 mL/min (165 bar) for 10 min; detector, 254 nm]: t_R = 2.3 min (mesitylene), 3.3 min (**3**), 7.5 min (*anti*-**4**), 9.0 min (*syn*-**4**). All concentrations are corrected to that of mesitylene at t_0 by equations, for example, $[anti\text{-}4]_t = \{f_{anti-4}F_{(anti-4)t}[Mes]_0\}/\{F_{(Mes)t}\}$. The necessary UV−HPLC factors (e.g., f_{anti-4}) are determined externally by ^{1}H NMR (200 MHz, $CDCl_3$). Runs were made at 1.0 and 3.0 kbar in the 7-kbar high-pressure autoclave. The corrected data of concentrations are available in Tables 60, 61, and 62 of ref 28, while the resulting calculated specific rate constants are given in Table 4.

Acknowledgment. W.v.E.D. thanks Professors Michael Henchman and Colin Steele for stimulating and illuminating discussions, and Dr. Lily Birladeanu for valuable assistance in the preparation of the manuscript. Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for the partial support of this work (J.L.E.), and to the National Science Foundation, Grant CHE-88 16186. J.L.E. expresses his thanks to Yale University for the award of a NASA traineeship. Funding of the Harvard University Mass Spectroscopy Laboratory by the National Institutes of Health (RR06716) and the National Science Foundation (CHE 90 20043) is gratefully acknowledged. F.-G.K. expresses his thanks to the Deutsche Forschungsgemeinschaft, the Ministry for Science and Research of the Land Nordrhein-Westfalen, and the Fond der Chemischen Industrie for support. This paper is dedicated to Professor Richard Neidlein on the occasion of his 70th birthday.

Supporting Information Available: Various tables and figures as indicated throughout the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA004128S

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