Thermally Promoted Ring Cleavage Reactions of Stereoisomeric Tetracyclo[4.3.0.0^{2,5}.0^{7,9}]non-3-enes, Pentacyclo[5.3.0.0^{2,6}.0^{3,5}.0^{8,10}]decanes, and Their Epoxide Counterparts

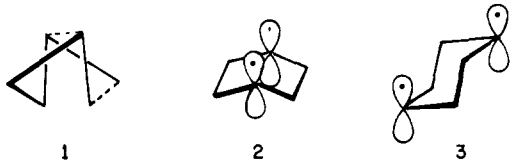
Leo A. Paquette* and Michael J. Carmody

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received March 22, 1976*

Abstract: The thermal isomerization of four tetracyclo[4.3.0.0^{2,5}.0^{7,9}]non-3-enes and four pentacyclo[5.3.0.0^{2,6}.0^{3,5}.0^{8,10}]decanes has been studied in benzene solution and the kinetics and stereochemistry of the rearrangements determined. The activation parameters derived from the rate constants reveal that replacement of cyclopropane methylenes by epoxide oxygens exerts no discernible effect on $\Delta H^{\ddagger}$ and E_a within either stereoisomeric subset. The energetic demands for the syn series were invariably less than those required of the anti compounds, presumably as a direct consequence of the greater ground-state strain in the syn isomers. Product studies revealed conversion to *trans*-1,5-bishomocyclooctatetraene and *trans*-1,5-diepoxycyclooctatetraene to be followed by both pentacyclic structural types. The tetracyclic compounds gave rise to homocyclooctatetraene and epoxycyclooctatetraene. The kinetic and stereochemical data are taken as evidence for central bond cleavage to generate boat 1,4-cyclohexanediyls, which undergo cleavage of the neighboring bicyclo[2.1.0]pentane bond to generate (*Z*,*Z*) dienes, which are capable of Cope rearrangement to deliver the observed products.

For the thermal fragmentation of saturated four-membered rings to be concerted, orbital symmetry dictates that a severely twisted geometry must be adopted.[1] This distortion requires two carbon atoms destined to become π-bonded partners to undergo rotation by roughly 180°, while the other two remain relatively fixed. On this basis, highly stereoselective *single* inversion of stereochemistry, the $_{\sigma}2_s + {}_{\sigma}2_a$ pathway, should result. Because little stereoselectivity has been observed in the pyrolytic cleavage of stereochemically labeled alkylcyclobutanes,[2] antarafacial motion in one developing olefinic moiety is evidently not readily achieved. Pretwisting of the incipient π orbitals in orthogonal fashion surprisingly also remains inadequate in promoting suprafacial-antarafacial cycloreversion.[3] In combination with extensive kinetic data, these experimental findings have proven most consistent with the intermediacy of singlet 1,4-butanediyl biradicals.[4]

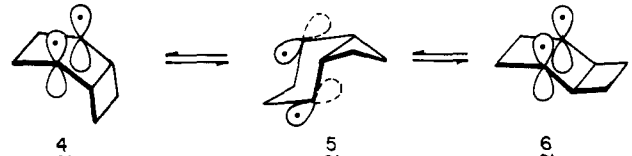
The structural features particular to the bicyclo[2.2.0]-hexane nucleus are even less conducive to concerted cleavage with formation of 1,5-hexadiene derivatives, since concomitant distortion of both cyclobutane rings as in **1** is required in the



1 **2** **3**

transition state.[5] The experimentally determined activation energy for thermochemical opening of the parent hydrocarbon (36 kcal/mol)[6] corresponds exactly to theoretical estimates based upon diradical intervention.[4d] More recent kinetic studies involving a series of 1,4-disubstituted bicyclo[2.2.0]-hexanes are fully supportive of a stepwise rearrangement process.[7] However, the relevant stereochemical findings are that high levels of antarafaciality are in fact attained by one of the double bonds.[5,8] Although such unprecedented configurational crossover would normally argue convincingly for the concerted $_{\sigma}2_s + {}_{\sigma}2_a$ alternative, a two-step process involving a singlet biradical relay[5] is now considered to be a more consistent interpretation. Thus, homolytic rupture of the weak bridgehead bond leads initially to boat 1,4-cyclohexanediyl **2**, internal rotation in which generates thermodynamically favored chair conformer **3**, which serves as precursor to 1,5-hexadiene product. Requisite stereochemical permutation and proper orientation of a second σ bond with the existing pπ orbitals are thereby achieved. The intervention of **2** also accounts for the susceptibility of bicyclo[2.2.0]hexanes to ring inversion.[8,9]

Pyrolyses of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octanes also follow the suprafacial-antarafacial pathway,[10] at least in certain instances.[11] The adapted explanation for these observations provides for initial generation of either **4** or **6**, de-



4 **5** **6**

pending upon the stereochemical parentage, followed by conformational ring inversion to **5**, which delivers (*Z*,*E*)-cycloocta-1,5-diene product. Despite the general acceptance of this rationalization for explaining the stereoselectivity of such cleavage reactions,[12] the intercession of conformationally distinctive biradical intermediates remains but a deductive assumption. Accordingly, further insight into this mechanistic question seemed highly desirable. This paper reports the results of a study in which both the $_{\sigma}2_s + {}_{\sigma}2_a$ mechanism and the boat to chair inversion process are blockaded by microcyclic annulation of the *syn*- and *anti*-tricyclooctadiene frames. Restriction of the energy surface in this manner was expected to alter the steric course from antarafacial to suprafacial regardless of the mechanism prevailing in the lesser restricted cases. The problem can be restated briefly as an examination of whether stereospecific (*Z*,*Z*) ring opening of pentacyclic molecules such as **7** and **8** might now be realized. The three-

7 **8**

membered ring appendages not only impose a suitable level of conformational constraint, but also introduce the requisite degree of stereochemical labeling. Because the kinetics of these cycloreversions also gain considerable importance, the rates of thermal reorganization of the stereoisomeric tetracyclo[4.3.0.0^{2,5}.0^{7,9}]non-3-enes and their 8-oxa analogues have been measured too. This last group of compounds represents a systematic link between the tricyclic and pentacyclic series.

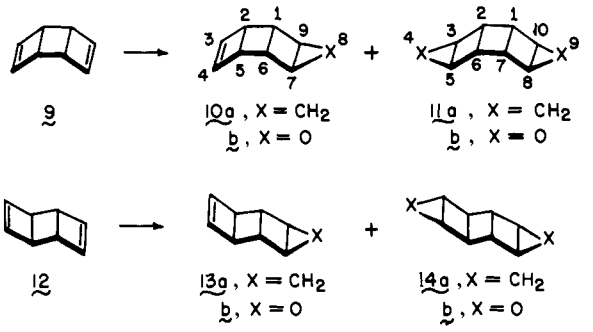
Table I. ^{1}H NMR Chemical Shift Data (δ, $CDCl_3$ solution)

Compd	Olefinic	Bicyclo[2.2.0] bridges		Bicyclo[2.1.0] bridges		Methylene groups	
		Allylic	Saturated	Cyclopropyl	Oxiranyl	Anti	Syn
			A. Tetracyclononenes				
10a	6.42 (m, 2 H)	3.32 (m, 2 H)	2.31 (m, 2 H)	1.43 (m, 2 H)		0.68 (d of t, J = 5 and 4.5 Hz, 1 H)	0.39 (d of t, J = 4.5 and 1.5 Hz, 1 H)
13a	6.30 (m, 2 H)	3.21 (m, 2 H)	2.19 (m, 2 H)	1.63 (m, 2 H)		0.87 (d of t, J = 5 and 4.5 Hz, 1 H)	0.42 (d of t, J = 4.5 and 1.5 Hz, 1 H)
10b	6.39 (d, J = 1 Hz, 2 H)	3.43 (d, J = 1 Hz, 2 H)	2.79 (dd, J = 4 and 8 Hz, 2 H)		3.83 (d, J = 4 Hz, 2 H)		
13b	6.31 (m, 2 H)	3.20 (m, 2 H)	2.69 (m, 2 H)		3.89 (d, J = 3.5 Hz, 2 H)		
			B. Pentacyclodecanes				
11a			2.50 (m, 2 H)	2.00 (d, J = 5 Hz, 4 H)		0.60 (d of t, J = 5 and 4.5 Hz, 2 H)	0.35 (d of t, J = 4.5 and 1.5 Hz, 2 H)
14a			2.42 (m, 4 H)	1.58 (d, J = 5 Hz, 4 H)		0.73 (d of t, J = 5 and 4.5 Hz, 2 H)	0.41 (d of t, J = 4.5 and 1.5 Hz, 2 H)
11b			2.80 (m, 4 H)		4.12 (m, 4 H)		
14b			2.78 (d, J = 3.5 Hz, 4 H)		3.94 (d, J = 3.5 Hz, 4 H)[a]		

[a] Additional fine coupling is apparent.

Results

Synthesis. The starting *syn*- (**9**) and *anti*-tricyclooctadienes (**12**) can be prepared conveniently by slight modification of Nenitzescu's method.[11b] Under his conditions, treatment of *cis*-3,4-dichlorocyclobutene with lithium amalgam in ether resulted in ready conversion to **12**. In contrast, we found the effectiveness of sodium amalgam under entirely comparable circumstances to be greatly reduced and to require prohibitively long reaction periods (ca. 2 weeks). Through the use of 25% HMPA in ether as solvent, however, conversion to **9** was complete in 7 h. When exposed to ethylzinc iodide and diiodomethane,[13] the preferred cyclopropanating agent in this work, both **9** and **12** afforded mixtures of mono and bis adducts which could be conveniently separated by VPC techniques. Greater control of product formation was realized with *m*-chloroperbenzoic acid, 1 equiv of reagent providing chiefly **10b** and **13b**. Diepoxides **11b** and **14b** were obtained through use



of excess peracid. These latter materials are not especially amenable to gas chromatography, but can be purified by standard column methods.

Stereochemical assignment to the various products follows principally from simple steric considerations and spectral data. Given the numerous NMR studies on bicyclo[2.1.0]pentanes,[14] some involving detailed computer simulation,[15] much detailed information on long-range coupling and shielding effects is available. For example, it is now recognized that the endo cyclopropyl proton generally experiences shielding relative to its exo counterpart as a consequence of its proximity to the cyclobutane ring.[14b,15,16] Marked shielding of the endo cyclobutyl hydrogens by the three-membered ring has also been demonstrated in these systems.[14b,15,17] Vicinal coupling constants in bicyclopentanes follow the Karplus relationship and have in general been accepted as diagnostic of stereochemistry.[18]

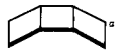
In the present work, it is especially noteworthy that the ^{1}H (Table I) and ^{13}C NMR spectra (Table II) of bis adducts **11** and **14** are compatible only with structures having symmetrically disposed X groups. Furthermore, the ready chemical elaboration of **11** and **14** from tetracyclic compounds **10** and **13**, respectively, requires that the small ring incorporated in these precursor molecules possess identical stereochemistry with *both* newly fused rings in the pentacyclodecanes. Since the multiplicities of $H_{3,5}$ and $H_{8,10}$ in **11a** and **14a** make it clear that very low levels of spin-spin coupling (<0.5 Hz) to bridge protons $H_{2,6}$ and $H_{1,7}$ are operative, these pairs of hydrogens must be geometrically fixed in an anti relationship. The substantial deshielding experienced by the saturated bicyclo[2.2.0]hexyl bridge protons upon replacement at X of CH_2 by O ($\Delta\delta$ = 0.30–0.48, Table I) likewise accords fully with exo orientation of the heteroatoms.[19] This effect is also reflected in the ^{13}C chemical shifts, although to a lesser degree. Noteworthy also are the consistently greater ^{13}C–H coupling constants exhibited by the central carbons of **10** and **11** relative to those of **13** and **14**, in agreement with the greater inherent s-orbital character of these bonds in the more highly strained syn series.[20]

Kinetics. The isomerizations of **10a, 13a,** and **13b** were studied kinetically and the results are presented in tabular form together with available quantitative information relating to the saturated and unsaturated tricyclooctanes (Table III). The pyrolyses were conducted in benzene solution on aliquots sealed in Pyrex tubes, and the progress of reaction was monitored by VPC analysis. Because of the extreme sensitivity of epoxide **10b** to trace impurities and the like, rate data were not determined for this compound. Good first-order dependence through two half-lives was obtained for all compounds and Arrhenius parameters together with standard deviations were derived by the method of least squares. In line with earlier thinking,[12b] the difference in E_a observed between **10a** and **13a** (4.7 kcal/mol) is seemingly associated with the greater steric strain in

Table II. ^{13}C NMR Chemical Shift Data (ppm from Me_4Si, $CDCl_3$ solution, 22.6 MHz)

		Bicyclo[2.2.0] bridges		Bicyclo[2.1.0] bridges		
Compd	Olefinic	Allylic	Saturated	Cyclopropyl	Oxiranyl	Cyclopropyl
10a	139.85 (167.2)	42.73 (158.9)	38.04 (148.9)	15.65 (180.7)		10.41 (159.1)
13a	140.71 (166.2)	50.07 (152.6)	44.57 (156.3)	17.97 (174.6)		13.16 (136.7)
11a			38.95 (147.7)	16.24 (175.8)		12.09 (163.6)
14a			46.40 (144.0)	17.70 (174.6)		11.28 (156.3)
11b			41.73 (153.8)		54.84 (197.8)	
14b			47.32 (151.1)		55.68 (205.1)	

Table III. Rate Constants and Activation Parameters for the Thermal Rearrangement of the Tetracyclo[4.3.0.$0^{2,5}$.$0^{7,9}$]nonenes and Related Compounds

Compd	T, °C	$k \times 10^5$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	log A
10a	90.4	4.37 ± 0.07	28.97 ± 0.76	0.81 ± 2.04	29.64 ± 0.59	13.51 ± 0.35
	100.0	12.01 ± 0.52				
	110.2	36.59 ± 1.22				
13a	119.8	3.40 ± 0.09	33.64 ± 0.22	6.11 ± 0.56	34.33 ± 0.34	14.69 ± 0.02
	130.2	10.48 ± 0.26				
	140.1	29.72 ± 0.79				
13b	120.3	7.71 ± 0.10	31.18 ± 0.80	1.37 ± 1.99	32.09 ± 0.69	13.76 ± 0.38
	130.1	19.98 ± 0.19				
	140.1	54.83 ± 0.71				
 [a]			30.9	3.4	31.7	13.6
 [a]					30.49 ± 0.16	14.22 ± 0.09
 [b]			31.2	4.1	32.1	13.3
 [b]					32.59 ± 0.17	14.01 ± 0.09

[a] Reference 11c. [b] Reference 12b.

Table IV. Rate Constants and Activation Parameters for the Thermal Rearrangement of the Pentacyclo[5.3.0.0^{2,6}.0^{3,5}.0^{8,10}]decanes

Compd	T, °C	$k \times 10^5$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	log A
11a	99.8	3.00 ± 0.07	30.68 ± 0.99	2.71 ± 2.55	31.38 ± 0.93	13.94 ± 0.53
	110.2	10.43 ± 0.19				
	130.2	74.81 ± 1.12				
11b	110.9	2.88 ± 0.05	29.22 ± 0.63	−3.71 ± 1.61	29.78 ± 0.50	12.46 ± 0.28
	120.0	6.92 ± 0.44				
	129.7	18.05 ± 0.40				
14a	159.6	4.43 ± 0.07	35.6	3.0	36.52 ± 2.96	14.12 ± 1.47
	170.0	10.43 ± 0.19				
	180.3	30.61 ± 0.99				
14b	129.7	1.31 ± 0.04	35.14	5.81 ± 2.12	36.01 ± 1.02	14.71 ± 0.54
	140.0	3.90 ± 0.10				
	149.9	11.39 ± 0.37				

the syn isomer, which increases its ground-state energy. The unsubstituted tricyclooctadienes, which isomerize smoothly to cyclooctatetraene in the gas phase, also feature activation parameters which are larger in the case of the anti example (ΔE_a = 2.1 kcal/mol).[12b] In the fully saturated series, the magnitude of this gap appears to be significantly lessened, although the kinetic measurements on which this conclusion is based are less extensive.[11c] Nevertheless, it is plausible that saturation of these tricyclic ring systems minimizes the differences in their strain energies. Certainly, any repulsive through-space interaction of the π bonds[21] is no longer operative.

The kinetic data for thermal rearrangement of the four pentacyclodecanes (Table IV) can also be reconciled on the basis of this rationalization. In this series, the rate constants for the pair of hydrocarbons were determined as before, but NMR techniques (in benzene-d_6) were utilized for the diepoxides because of the limited stability of both starting materials and products to gas chromatographic conditions. An important second feature of these thermolyses was now made manifest. Specifically, replacement of the cyclopropane methylene groups by epoxide oxygen atoms is seen to exert no experimentally discernible effect on $\Delta H^{\ddagger}$ and E_a within either stereoisomeric subset. Since existing precedent[22] suggests that rate-determining rupture of an internal cyclopropane or oxirane σ bond would be characterized by a substantially higher activation energy for the oxygenated derivative, it would appear safe to proceed on the assumption that a more centrally positioned cyclobutane bond is experiencing initial cleavage. Although a more thorough discussion of this point is deferred to a later section, we note at this time that the activation energies in Tables III and IV fall into a nicely cohesive pattern on the strength of this mechanistic reasoning.

Product Studies. Thermal activation of **10a** at 100 °C for 6 h resulted in initial isomerization to *cis*-bicyclo[6.1.0]-nona-2,4,6-triene which, because of its lability to heat, underwent concomitant rearrangement to an ca. 85:15 mixture of *cis*- and *trans*-8,9-dihydroindene.[23] At the more elevated temperature required for pyrolysis of **13a** (130 °C), exclusive conversion to *cis*-8,9-dihydroindene was realized. In compa-

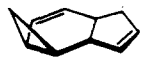
rable experiments, the structurally related epoxides **10b** and **13b** were observed to give high yields of cyclooctatetraene oxide.

The thermal chemistry of **11a** is characterized by ready conversion to diene **15,** whose structural assignment follows

15a ⇌ 15b

from its temperature-dependent ^1H and ^{13}C NMR spectra. Ring inversion in this stereoisomer returns the identical molecule, but with interchange of the chemical environments of the 12 constituent protons and all ten carbon atoms. When the exchange process becomes rapid on the NMR time scale, extensive averaging results. The free energy of this degenerate ring inversion, determined to be 16.4 kcal/mol,[24] establishes the process as quite facile. This behavior differs intrinsically from that expected of *cis*-1,5-bishomocyclooctatetraene, where conformational inversion now generates a nonidentical structure. Additionally, as its two methylene groups are transposed from the extended to the folded form, high-order steric congestion develops representing a much less favorable and more energy demanding state of affairs than found in **15**.

Diene **15** was also isolated from the pyrolysis of **14a,** but much polymer was produced as well at the higher temperature required for rearrangement (170 °C). This is almost certainly not the direct result of product decomposition, since pure **15** undergoes smooth first-order isomerization under these conditions to a product believed to be **16** on the basis of spectral



16

data. This vinylcyclopropane → cyclopentene bond reorganization operates to the exclusion of epimerization in **15**.[25] The ^1H NMR spectrum (in C_6D_6)[26] of this 2-norcarene derivative consists of a low-field multiplet at δ 6.0–6.2 and a doublet of doublets (J, 9.5 and 2 Hz) centered at 5.22 due to the α and β protons, respectively, and two multiplets at 0.6 and 1.1 arising from the geminal cyclopropyl hydrogens. The cyclopentene olefinic pair is seen as a pseudosinglet at δ 5.8 and the remaining sp^3-bound protons give rise to multiplets in the 1.2–3.7 region. The features of these signals were not sufficiently first order to permit unequivocal assignment of stereochemistry to the ring juncture.

The structurally related diepoxide **14b** was more well behaved, being converted exclusively to **17** at 150 °C. Rearrangement of **11b** proceeded at a somewhat lower temperature (130 °C) to give chiefly **17** (~95%) with light contamination by **18** (~5%). These stereoisomers are readily distinguished by their ^1H NMR spectra.[27] We and others[27] have shown that **17** and **18** are not interconverted at these temperatures. Nor

17 18

is this the case with **15** and its cis isomer. On this basis, the possibility that *cis*-1,5-bishomocyclooctatetraene and **18** are kinetically controlled products and that **15** and **17** are the thermodynamically controlled ones can seemingly be dismissed. Rather, the experimental results suggest that both sets of pentacyclic molecules undergo thermal rearrangement through one of two common intermediates, which lead directly to **15** or **17**.

The adherence by these molecules to good first-order kinetics establishes, of course, that the slower reacting of the two isomers (e.g., **14a** and **14b**) cannot serve as an intermediate in the rearrangement of the faster (**11a, 11b**). Careful monitoring of the early and later stages of the thermal isomerizations of **14a** and **14b** provided no indication of their prior rearrangement to **11a** and **11b,** respectively. Intervention of the faster isomers cannot be excluded on this basis, but we simply point out that such chemical changes require the cleavage-recombination of two internal bonds.

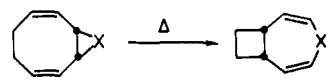
Related to this question in a mechanistic sense is the realization that the conversions of **11a** to **15** and of **11b** to **17** involve configurational inversion of two adjoining bicyclo[2.1.0]pentyl bridgehead sites. For **14a** and **14b,** the pair of relevant protons are preoriented in an anti relationship and the conversion to ring opened products in these two cases proceeds formally with full retention.

Discussion

Since synchronous bond fission at $C_{1,7}$ and $C_{8,10}$ (or the equivalent $C_{2,6}$; $C_{3,5}$ sites—see formula **11** for numbering) can be excluded on an a priori basis because of poor orbital geometry, there remains to distinguish between product-determining cleavage of the two central bicyclo[2.2.0]hexane bonds or a biradical process in which homolysis of a bicyclo[2.1.0]pentane bond gains importance. As concerns the first of these processes, earlier precedent[10] would indicate that dienes having (*E,Z*) double bonds might arise under conditions of kinetic control in certain examples. Otherwise, the (*Z,Z*) isomers could be formed directly. Given the strain level in such (*E,Z*)-1,5-bishomocyclooctatetraenes, rapid geometric isomerization to the thermodynamically favored (*Z,Z*) dienes becomes a very likely event.[10] Since the relative stereochemical disposition of the three-membered rings would not be thereby affected, compounds **11a** and **11b** would serve as precursors to *cis*-1,5-bishomocyclooctatetraenes, while **14a** and **14b** would generate the trans counterparts. This is fully inconsistent with the product studies which reveal trans-fused products to predominate heavily under conditions where the cis isomers prove stable (and vice versa). This mechanistic viewpoint is therefore considered as untenable.

Assuming the behavior of **19** ($\Delta\Delta H^{\ddagger}$ = 3.3) and **20** ($\Delta\Delta H^{\ddagger}$ = 3.6) to provide serviceable analogy,[22] then the enthalpies of activation for the oxygen heterocycles should be of appreciably greater magnitude than those of structurally related hydrocarbons if internal bicyclo[2.1.0]pentane bond cleavage is kinetically important. In actual fact, the activation parameters within each stereoisomeric subset are less disparate than the above: for **13a/13b,** $\Delta\Delta H^{\ddagger}$ = 2.46; **11a/11b,** 1.46; and **14a/14b,** 0.46. Given the error limits of these measurements, the deviations are seen to be insufficiently meaningful to permit firm mechanistic conclusions.

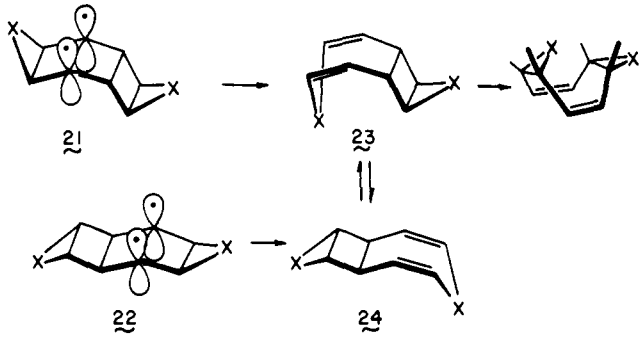
19a, X = O; $\Delta H^{\ddagger}$ = 22.7 kcal/mol
b, X = CH_2; $\Delta H^{\ddagger}$ = 19.4 kcal/mol



20a, X = O; $\Delta H^{\ddagger}$ = 28.6 kcal/mol
b, X = CH_2; $\Delta H^{\ddagger}$ = 25.0 kcal/mol

However, it is clear that members of the syn series experience ring opening more readily than their anti counterparts, in line with their greater intrinsic strain. This kinetic effect seems best accommodated by homolysis of an internal bicy-

clo[2.2.0]hexyl bond ($C_{1,7}$ or $C_{2,6}$) with generation of biradical species such as **21** and **22** because of its close parallelism with the behavior of the parent tricyclic systems (Table III). In contrast to the capability of biradicals **2, 4,** and **6** for facile conformational inversion to their chair forms, these boat-like cyclohexanediyls are rigid intermediates wherein bond rotation is precluded from operating because of the structural constrains imposed by the two three-membered rings. In operational terms, this blockade of the normal ring flip can provide for subsequent disrotatory opening of the neighboring bicyclo[2.1.0]pentane bond and formation of (*Z,Z*) dienes **23** and **24**. Although **23** and **24** are generated in distinctive con-



formations, these representations nevertheless comprise a single chemical species. Consequently, if the syn and anti isomers do not experience prior structural interconversion, it would be at this stage that their identities would be lost. Simple ring inversion in extended conformation **24** provides the somewhat more sterically demanding coiled form **23** necessary[28] for the Cope rearrangement, which would deliver the products ultimately observed.

The combined weight of the above kinetic and stereochemical data forms the basis for our conclusion that a biradical energy surface is reached. The homolysis mechanism may be followed in our examples because of the special steric prohibition of the $_{\sigma}2_a + {}_{\sigma}2_s$ fragmentation, but need not be the most energetically accessible pathway operating during thermal cleavage of simpler fused cyclobutanoid systems.

Experimental Section

The ^{1}H NMR spectra were obtained with Varian T-60, Varian A-60A, and Jeolco MH-100 spectrometers and apparent splittings are given in all cases. A Bruker 90 spectrometer was employed for the recording of ^{13}C spectra. Mass spectral measurements were made on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***syn*-Tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (9).** A solution containing 12.3 g (0.10 mol) of *cis*-3,4-dichlorocyclobutene[29] in 200 ml of dry ether and 60 ml of anhydrous hexamethylphosphoramide was added under nitrogen to 650 g of 0.5% sodium amalgam contained in a 500-ml three-necked Morton flask equipped with a mechanical stirrer, nitrogen inlet, and addition funnel. The mixture was stirred vigorously for 7 h, the ethereal solution decanted, and the amalgam washed with ether (2 × 100 ml). The combined ether layers were filtered through Celite and the major portion of solvent removed by distillation through a Vigreux column. The remaining ether was removed at 0 °C (40 mm) and the hydrocarbon obtained by raising the temperature to 40 °C. There was isolated 1.8 g (34.6%) of **9** having spectral properties identical with those reported.[11b]

1β,2β,5β,6β,7α,9α-Tetracyclo[4.3.0.0^{2,5},0^{7,9}]non-3-ene (10a) and 1β,2β,3α,5α,6β,7β,8α,10α-Pentacyclo[5.3.0.0^{2,6},0^{3,5},0^{8,10}]decane (11a). To a magnetically stirred solution of ethylzinc iodide (50 ml, 1 M, 50 mmol) contained in a 250-ml three-necked flask equipped with condenser, addition funnel, and gas inlet tube was added dropwise under nitrogen 5.35 g (20 mmol) of diiodomethane dissolved in 10 ml of anhydrous ether. This solution was heated at reflux for 1 h and cooled, while 1.04 g (10 mmol) of **9** and 5.35 g of diiodomethane dissolved in 15 ml of ether was added dropwise. After an additional 9 h at the reflux temperature, the reaction mixture was cooled and poured into ice-cold saturated ammonium chloride solution. The organic phase was dried and concentrated in vacuo to leave a pale yellow oil consisting of two compounds in a 55:45 ratio. These were separated by preparative VPC (5% SE-30 on Chromosorb G, 70 °C). The more rapidly eluted component was identified as **10a**; *m/e* calcd 118.0782, found 118.0783.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.25; H, 8.73.

The product of longer retention time proved to be **11a**; *m/e* calcd 132.0939, found 132.0935.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.91; H, 9.32.

8-Oxa-1β,2β,5β,6β,7α,9α-tetracyclo[4.3.0.0^{2,5},0^{7,9}]non-3-ene (10b). A mechanically stirred solution of 1.0 g (9.6 mmol) of **9** in 20 ml of dichloromethane was treated dropwise with 1.82 g (10.6 mmol) of *m*-chloroperbenzoic acid dissolved in 75 ml of the same solvent. After 1 h the reaction mixture was poured into 200 ml of water and the dichloromethane layer brought to equal volume. The organic phase was separated, washed with saturated sodium bicarbonate solution (2 × 50 ml), water (50 ml), and brine (50 ml), dried, and evaporated. The residual oil was chromatographed on Florisil (elution with 15% ether in pentane) to give 700 mg (47%) of **10b** as a waxy white solid, mp 31–32 °C (after sublimation); *m/e* calcd 120.0575, found 120.0577.

4,9-Dioxa-1β,2β,3α,5α,6β,7β,8α,10α-pentacyclo[5.3.0.0^{2,6},0^{3,5},0^{8,10}]decane (11b). To a magnetically stirred solution of **9** (900 mg, 9.0 mmol) in ether (10 ml) cooled to −20 °C under nitrogen was added dropwise 45 ml of 0.5 *N* monoperphthalic acid in ether (32 mmol). The mixture was allowed to warm to room temperature, where stirring was continued for 17 h. The phthalic acid was separated by filtration and washed with ether. The combined organic layers were processed as above to leave a white solid. Additional product was isolated by continuous dichloromethane extraction of the first bicarbonate wash. The combined solids were sublimed (60 °C, 0.1 mm) to furnish 610 mg (49%) of **11b**, mp 141–142 °C, after sublimation.

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.74; H. 6.09.

1β,2α,5α,6β,7α,9α-Tetracyclo[4.3.0.0^{2,5},0^{7,9}]non-3-ene (13a) and 1βb,2α,3β,5β,6α,7β,8α,10α-Pentacyclo[5.3.0.0^{2,6},0^{3,5},0^{8,10}]decane (14a). Treatment of **12** (2.5 g, 24 mmol) and diiodomethane (13.5 g, 48 mmol) in 50 ml of ether with a reagent prepared from 100 ml of 1 M ethereal ethylzinc iodide and 13.5 g of diiodomethane (reflux 1 h) according to the predescribed procedure afforded a mixture comprised of unreacted **12, 13a,** and **14a**. The components were separated by preparative VPC (5% XF-1150 on Chromosorb G, 50 °C). Monoolefin **13a** was obtained as a colorless oil, 470 mg (23%); *m/e* calcd 118.0782, found 118.0783.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.19; H, 8.32.

There was also isolated 900 mg (28%) of **14a**; *m/e* calcd 132.0939, found 132.0942.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.42; H, 9.47.

8-Oxa-1β,2α,5α,6β,7α,9α-tetracyclo[4.3.0.0^{2,5},0^{7,9}]non-3-ene (13b) and 4,9-Dioxa-1βb,2α,3β,5β,6α,7β,8α,10α-pentacyclo[5.3.0.0^{2,6},0^{3,5},0^{8,10}]decane (14b). To a magnetically stirred solution of 1.04 g (10 mmol) of **12** in 10 ml of ether cooled to −20 °C was added dropwise 15.4 ml of ethereal 0.65 *N* monoperphthalic acid. The solution was allowed to warm to room temperature, where after 8 h the phthalic acid was separated by filtration and washed with ether. Workup in the predescribed manner left a white paste, chromatography of which on Florisil (elution with pentane–ether 4:1) furnished 300 mg (25%) of **13b** and 380 mg (28%) of **14b**.

The monoepoxide was an oil; *m/e* calcd 120.0575, found 120.1577.

The diepoxide was obtained as colorless crystals, mp 111–112.5 °C after sublimation; *m/e* calcd 136.0524, found 136.0526.

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.47; H, 5.89.

Kinetic Measurements. A. NMR Method. A standard solution of the diepoxide (300 mg) in 1.5 ml of dry benzene-d_6 was prepared and 250-μl aliquots were introduced into NMR tubes which had been pretreated in turn with 10% nitric acid, 10% ammonium hydroxide, water, and acetone prior to oven drying at 70 °C. The tubes were

sealed at −78 °C and 15 mm before immersion in an oil bath preheated to the appropriate temperature. The tubes were removed individually at appropriately timed intervals, cooled to 0 °C, and the ^{1}H spectra recorded at ambient temperature. The amount of residual starting material at any given time was determined by suitable integration of the >C*H*O- signals in the original epoxide and product. Plots of $\ln a/(a-x)$ vs. time (s) were linear through two half-lives. Least-squares treatment of these plots provided the data in Table IV.

B. VPC Method. Standard solutions were prepared by dissolving the substrate (50 mg) and internal standard (50 mg) in 5 ml of dry benzene. For the tetracyclononenes, the internal standard was *n*-decane, while cyclododecane and cyclodecane were utilized for the **11a**/**14a** pair and **13b**, respectively. Into prewashed (see above) Pyrex tubes were introduced 25-μl aliquots of the solutions. The tubes were sealed and manipulated as above, except that the progress of reaction was monitored by flame ionization VPC.

Preparative Scale Thermolysis of the Tetracyclononenes. A. Syn Isomer 10a. A 30-mg sample of **10a** was dissolved in benzene-d_6 and its signals integrated with respect to the residual benzene protons. After heating at 110 °C for 15 000 s ($10\ t_{1/2}$), the ^{1}H NMR spectrum was shown to be superimposable upon that of the mixture obtained upon heating *cis*-bicyclo[6.1.0]nonatriene under the same conditions. The conversions were both essentially quantitative. VPC analysis of the two product mixtures revealed the composition to consist of an 85:15 ratio of *cis*- and *trans*-8,9-dihydroindene.

During the kinetic runs which were monitored by VPC, a peak was seen to gain prominence during the first half-life of **10a**, reach a maximum at $t_{1/2}$, and gradually transmute to the dihydroindenes. The retention time of this material was identical with that of *cis*-bicyclo[6.1.0]nonatriene on several columns.

Anti Isomer 10b. The runs were carried out as above, but at a somewhat higher temperature (150 °C.). No *cis*-bicyclo[6.1.0]nonatriene could now be observed because of the necessarily higher temperatures.

Preparative Scale Thermolysis of 11a. A sample of **11a** (300 mg, 2.67 mmol) was dissolved in 3 ml of benzene and this solution was sealed into a thick-walled Pyrex ampule at −78 °C and 15 mm before immersion into an oil bath preheated to 150 °C. After 6 h, the tube was returned to −78 °C and opened. The single volatile component was isolated by preparative VPC on a 12 ft × 0.25 in. 15% XF-1150 column (Chromosorb W, 90 °C, 100 ml/min). There was obtained 250 mg (83%) of **15** as a colorless oil: $\delta_{Me_4Si}^{CDCl_3}$ 5.57 (br s, 4 H), 1.56 (m, 5 H), and 0.78-1.21 (m, 3 H); *m/e* calcd 132.0938, found 132.0942.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 9.31.

At −45 °C and below, the off-resonance decoupled ^{13}C NMR spectrum of **15** ($CDCl_3$ solution) consists of six lines: 128.35, 126.90, 22.71, 17.80, 16.51, and 14.02 ppm. As the temperature is raised, these signals at 127.62, 20.55, and 15.26 ppm. This mutual averaging of peaks shows that rapid equilibration between **15a** and **15b** leads to total environmental exchange between the four methine, four olefinic, and two methylene carbons. Matching of calculated (DNMR 2) and observed methylene and olefinic segments of these spectra provided a series of rates from which the following thermodynamic data were obtained: E_a, 16.41 kcal/mol; log A, 14.08; $\Delta H^{\ddagger}$, 16.17 kcal/mol; and $\Delta S^{\ddagger}$, −5.2 eu.

Because of limited quantities of materials, the remaining "preparative" scale experiments were conducted in one of two ways. In the first, 30 mg of the compound to be studied was dissolved in benzene-d_6 and this solution was sealed in a precleaned (see above) NMR tube. The spectrum was recorded and the various signals carefully integrated with respect to the residual benzene peak. The tube was then immersed in an oil bath preheated to the temperature utilized in the most rapid kinetic run and heating was continued for at least ten half-lives. The spectrum was recorded again and integrated as before to establish the extent of conversion. For **11b** and **14b**, >97% conversion to a single product was noted. The spectra were superimposable upon those of authentic products.

The second approach consisted of heating one ampule from the kinetic experiments for at least ten half-lives and performing a VPC analysis as above. For **13a** and **13b**, the conversions were quantitative; in the case of **14a**, the yield of **15** was determined to be 21%. Much polymer formation was in evidence.

Thermal Rearrangement of 15. A solution of **15** (55 mg, 0.41 mmol) in 1 ml of benzene was sealed in a Pyrex tube as described above and heated for 12 h at 170 °C. After cooling, the contents were removed and the single product isolated by preparative VPC on the XF-1150 column. There was obtained 48 mg (87%) of **16** as a colorless liquid; $\delta_{Me_4Si}^{CDCl_3}$ 6.0-6.2 (m, 1 H), 5.8 (br s, 2 H), 5.22 (dd, J = 9.5 and 2 Hz, 1 H), 3.45 (m, 1 H), 2.0-3.1 (br m, 3 H), 1.4 (m, 2 H), 1.1 (m, 1 H), and 0.6 (m, 1 H); ^{13}C NMR ($CDCl_3$) 135.64, 128.41, 127.98, 126.79, 42.14, 41.11, 34.58, 15.16, 14.19, and 9.55; *m/e* calcd 139.0939, found 132.0941.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.18.

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References and Notes

(1) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (b) A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 1671 (1969); (c) J. E. Baldwin and P. W. Ford, *J. Am. Chem. Soc.*, **91**, 7192 (1969); (d) L. A. Paquette and G. L. Thompson, *ibid.*, **93**, 4920 (1971); **94**, 7127 (1972).

(3) L. A. Paquette and M. J. Kukla, *Tetrahedron Lett.*, 1241 (1973).

(4) For exhaustive reviews, cf. (a) H. M. Frey, *Adv. Phys. Org. Chem.*, **4**, 147 (1966); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (c) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (d) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969); **2**, 423 (1970); (e) S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 21**, 14 (1970).

(5) L. A. Paquette and J. A. Schwartz, *J. Am. Chem. Soc.*, **92**, 3215 (1970).

(6) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

(7) (a) R. Srinivasan, *Int. J. Chem. Kinet.*, **1**, 133 (1969); (b) D. C. Owsley and J. J. Bloomfield, *J. Am. Chem. Soc.*, **93**, 782 (1971); (c) E. N. Cain, *Tetrahedron Lett.*, 1865 (1971); (d) E. N. Cain and R. K. Solly, *Int. J. Chem. Kinet.*, **4**, 159 (1972); *Aust. J. Chem.*, **25**, 1443 (1972); *J. Am. Chem. Soc.*, **94**, 3830 (1972); **95**, 4791, 7884 (1973).

(8) (a) M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, **94**, 5119 (1972); (b) A. Sinnema, F. van Rantwijk, A. J. deKoning, A. M. van Wijk, and H. van Bekkum, *J. Chem. Soc., Chem. Commun.*, 364 (1973).

(9) (a) The thermal rearrangement of bicyclo[2.2.0]hexane has recently been assessed theoretically: M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Am. Chem. Soc.*, **96**, 5242 (1974). (b) The stereochemistry of the thermal 2,3-dimethylbicyclo[2.1.0]pentane to 2,5-heptadiene isomerization reaction has also been examined: J. A. Berson, W. Bauer, and M. M. Campbell, *J. Am. Chem. Soc.*, **92**, 7515 (1970).

(10) (a) D. Bellus, H.-C. Mez, G. Rihs, and H. Sauter, *J. Am. Chem. Soc.*, **96**, 5007 (1974); (b) H.-D. Martin and E. Eisenmann, *Tetrahedron Lett.*, 661 (1975).

(11) (a) E. Vogel, O. Roos, and K.-H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 63 (1962); (b) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964); (c) H. Tanida, T. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341 (1969).

(12) The thermolysis of the syn and anti dimers of cyclobutadiene has likewise been interpreted in terms of a biradical mechanism, although some intersystem crossing to triplet species may now be involved: (a) R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegir, *J. Am. Chem. Soc.*, **96**, 7581 (1974); (b) H. M. Frey, H.-D. Martin, and M. Hekman, *J. Chem. Soc., Chem. Commun.*, 204 (1975).

(13) S. Sawada and Y. Inoue, *Bull. Chem. Soc. Jpn*, **42**, 2669 (1969).

(14) (a) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962); (b) W. R. Rot and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); (c) M. G. Waite, G. A. Sim, C. R. Olander, R. J. Warnet, and D. M. S. Wheeler, *J. Am. Chem. Soc.*, **91**, 7763 (1969); (d) J. J. Tufariello and A. C. Bayer, *Tetrahedron Lett.*, 3551 (1972).

(15) (a) K. B. Wiberg and D. E. Barth, *J. Am. Chem. Soc.*, **91**, 5124 (1969); (b) E. Block, H. W. Orf, and R. E. K. Winter, *Tetrahedron*, **28**, 4483 (1972).

(16) J. G. Traynham, J. S. Dehn, and E. E. Green, *J. Org. Chem.*, **33**, 2587 (1968).

(17) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **91**, 6766 (1969).

(18) F. A. Bovey, "Nuclear Magnetic Resonance," Academic Press, New York, N.Y., 1969.

(19) L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Am. Chem. Soc.*, **89**, 5246 (1967).

(20) For leading references, consult: (a) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Am. Chem. Soc.*, **94**, 997 (1972); (b) K. B. Wiberg, *Adv. Alicycl. Chem.*, **2**, 185 (1968); (c) M. Christl, *Chem. Ber.*, **108**, 2781 (1975).

(21) R. Gleiter, E. Heilbronner, M. Hekman, and H.-D. Martin, *Chem. Ber.*, **106**, 28 (1973).

(22) (a) J. C. Pommelet and J. Chuche, *Tetrahedron Lett.*, 3897 (1974); (b) J. C. Pommelet, N. Manisse, and J. Chuche, *Tetrahedron*, **28**, 3929 (1972); (c) J. M. Brown, B. T. Golding, and J. J. Stofko, *J. Chem. Soc., Chem. Commun.*, 319 (1973); (d) W. Grimme and K. Seel, *Angew. Chem., Int. Ed. Engl.*, **12**, 507 (1973).

(23) This ratio has previously been realized in the direct thermal rearrangement of *cis*-bicyclo[6.1.0]nonatriene at 90 °C: E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

(24) L. A. Paquette, M. J. Carmody, and J. M. Geckle, *Tetrahedron Lett.*, 2753 (1976).
(25) *cis*-1,5-Bishomocyclooctatetraene has been prepared by the direct cyclopropanation of cyclooctatetraene with diazomethane and cuprous chloride: W. W. Frey, Dissertation, Universitat zu Koln, 1966. When pyrolyzed in a sealed tube at the much higher temperature of 250 °C for 50–75 min, this tricyclic diene was partially converted to I, II (probable stereochemistry indicated), and two unidentified products. We are grateful to Professor Vogel for making a copy of the Frey dissertation available to us.

I

II

(26) L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, **37**, 3849 (1972).
(27) (a) A. G. Anastassiou and E. Reichmanis, *J. Org. Chem.*, **38**, 242 (1973); (b) D. P. Mullis, Ph.D. Thesis, University of California at Los Angeles, 1970.
(28) W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1967).
(29) R. Pettit and J. Henery, *Org. Synth.*, **50**, 36 (1970).

Pressure Dependence of the Thermolysis of Tetramethyl-1,2-dioxetane: the Volume of Activation and Its Mechanistic Implications

R. Schmidt, H.-C. Steinmetzer, H.-D. Brauer, and H. Kelm*

Contribution from the Department of Chemistry, University of Frankfurt, D 6000 Frankfurt am Main, West Germany. *Received March 12, 1976*

Abstract: The thermal decomposition of tetramethyl-1,2-dioxetane (TMD) and its indirect chemiluminescence via 9,10-dibromoanthracene (DBA) was studied in different solvents at pressures ranging from 1 to 1000 atm. The pressure dependence of the rate constants of decomposition of TMD at 60 °C permits the calculation of the volumes of activation, $\Delta V^{\neq}_{D}$, amounting to 9 ± 2 cm^3/mol in toluene and 11 ± 3 cm^3/mol in chlorobenzene. Apparent volumes of activation, $\Delta V^{\neq}_{Ch}$, were obtained from the pressure dependence of the intensity of chemiluminescence at 40 °C on the system TMD-DBA and amount to 8 ± 1 cm^3/mol in toluene, 10 ± 1 cm^3/mol in chlorobenzene, and 11 ± 2 cm^3/mol in benzonitrile, respectively. These data are discussed in connection with literature values for homolytic bond cleavages. They cannot exclude a biradical mechanism, but favor a concerted pathway for the decomposition. Partial molar volumes of the TMD and acetone in toluene were determined and a volume profile for the reaction is presented. Thus one can deduce that the transition state is placed much closer to the side of the educt.

Although substituted dioxetanes have been known for only several years,[1-3] their thermal decompositions, together with their direct or indirect chemiluminescence, are frequently investigated reactions.[4-7]

Using different methods to follow the thermal decomposition reactions, it was shown that they obey first-order kinetics in diluted, air-saturated solutions. The reactions are autocatalyzed, however, in degassed or concentrated solutions.[4,8,9] Transition metal ions catalyze the decomposition.[10,11] Products of the thermolysis of dioxetanes are the corresponding carbonyl compounds in their ground states as well as in their excited states, the latter being responsible for the appearance of the direct and indirect chemiluminescence.[7] According to product analysis and physical investigations, the product of the thermal decomposition of TMD was identified as acetone, of which ca. 50% is in its ground state, ca. 0.2% in its excited singlet state, and ca. 50% in its excited triplet state.[9,12]

The appearance of acetone in an electronically excited state can be understood, if one takes into account thermochemical data,[13] activation parameters of the thermolysis,[14] and thermodynamic considerations.[15] This possibility of transferring molecules into their electronically excited states by means of a chemical reaction rather than irradiation initiated a series of investigations about energy transfer processes and photochemical reactions.[5,16-21]

Despite the host of information on the thermolysis of TMD, the mechanism of the primary rate-determining step of the reaction is still ambiguous. Two mechanisms, schematically shown in Figure 1, are both being discussed. Mechanism A represents a one-step process with the synchronous cleavage of the carbon–carbon and the oxygen–oxygen bonds, whereas mechanism B consists of a two-step reaction including a biradical intermediate following the peroxide bond cleavage.

A very small observed solvent effect on the decomposition[10] excludes any mechanism involving polar transition states and/or intermediates. However, it is compatible with both mechanisms depicted in Figure 1. Applications of correlation diagrams with regard to symmetry rules[21-26] are consistent with a concerted mechanism. On the other hand, activation parameters in connection with thermochemical considerations[27-31] support the formation of a biradical. Recently a biradical mechanism for the decomposition of trimethyldioxetane was proposed by Stauff.[32]

With the present investigations further data on the kinetics and chemiluminescence of TMD thermolysis under pressure are presented and discussed in view of the possible mechanisms.

Experimental Section

Materials. TMD was prepared and purified as previously described.[17] The Aldrich-Europe product DBA was repeatedly recrystallized from ethanol for purification. Commercially available solvents like toluene, chlorobenzene, and benzonitrile of highest purity were redistilled before use. Additions of ethylenediaminetetraacetic acid (EDTA) to the solvents in order to complex any possibly present, and catalytically active, transition metal ions[10,30] showed no influence on the results.

High-Pressure Measurements of Thermal Decomposition and Luminescence. The thermolysis reaction of TMD was followed by recording the time dependence of the intensity of the indirect chemiluminescence of DBA, which is excited mainly by triplet-singlet energy transfer via triplet-excited acetone.[17] Air saturated solutions with