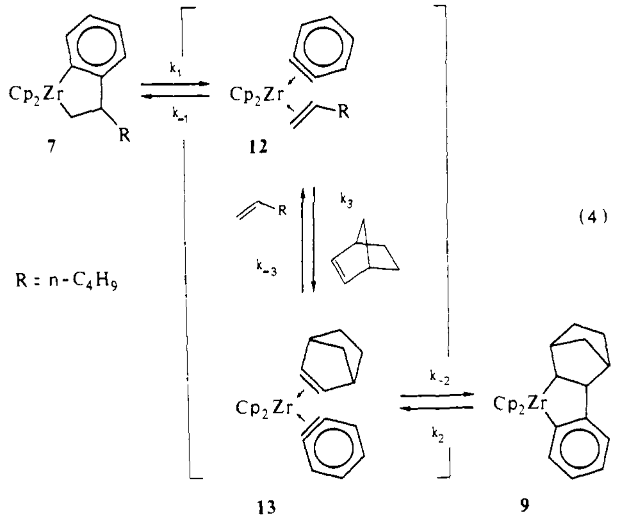
subjected to two different types of thermally induced reaction paths. The high activation energy process leading to phenylalkanes most likely does not reflect a reaction mode typical of a five-membered metallacycle. It rather resembles the thermal decomposition of acyclic group 4 transition metal-aryl complexes.[6,9] The loss of one deuterium atom from the aryl group, the isotopic scrambling of the already formed phenylalkane, and the participation of aromatic solvents in the reaction can sufficiently be accounted for by an intermediate aryne-zirconocene complex. The formation of such a species (e.g., **11** from **6**) by a β-hydride elimination from the aromatic ring is an attractive mechanistic possibility[10] (eq 3). A different intramolecular reaction pathway with a lower activation energy, however, becomes apparent in the presence of alkenes. In the thermolysis of the zirconaindans, a reactive intermediate is formed which can only revert to the starting material, if not intercepted by an added olefin. A reasonable structure of this intermediate is the 18-electron species aryne olefin zirconocene (e.g., **12** from **7**)[11] (eq 4). The introduction of the dehydrobenzene ligand into this type of intermediate, as expected, leads to an extraordinary high thermal stability of the corresponding five-membered metallacycle. Moreover, the initial ring opening of the metallaindan represents the rate-determining step in the reaction sequence (eq 4).[12] This feature can be used to obtain information about the influence of structural changes or substituent effects on the transformation between metallacyclic and bis(olefin) structure by this exchange reaction. The $\Delta G^{\ddagger}$ differences observed (Table I) reflect a pronounced influence of the olefinic ligand on the intermediate—the formation of the more strained olefins makes the ring opening of the metallacycle less favorable.[13] The unexpected deviation of **8** from this behavior seems to indicate the sensitivity of this reaction to steric hindrance, here introduced by the geminal two methyl groups.



The thermal reactions of the zirconaindans demonstrate that these metallacycles exhibit a reactivity which is markedly dependent on the substitution, but, nevertheless, still follow a reaction pattern typical of a five-membered metallacycle. The unique features of the equilibrium between metallacycle and bis(olefin) complex should make these readily available metallaindans useful model systems to study the influence of structural changes on carbon-carbon bond formation processes in transition metal complexes.

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(1) The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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(7) The description of **5** as 1-[bis(η^5-cyclopentadienyl)zircona]indan is consistent with its spectroscopic properties and chemical reactivity—reactions with protic acid, halogen, or carbon monoxide give products expected for the five-membered metallacycle: ^{1}H NMR (in C_6D_6) δ 7.20–6.55 (m, 4 H, aromatic), 5.95 (s, 10 H, cyclopentadienyl), 3.25 (t, 2 H, benzylic), 1.25 (t, 2 H); ^{13}C NMR (in C_6D_6) δ 183.8, 150.2, 136.8, 127.2, 125.6, 124.0 (6 C, aromatic), 112.0 (10 C, cyclopentadienyl), 43.0 (1 C, α to the metal), 34.4 (1 C, benzylic). The ^{1}H NMR spectrum of 3-methyl-1-zirconaindan (**6**) indicates a strong deviation of the five-membered ring from planarity:[8] δ 7.50–6.90 (m, 3 H), 6.65–6.30 (m, 1 H, aromatic), 5.95 (s, 5 H), 5.90 (s, 5 H, cyclopentadienyl), 3.50, 2.15, 0.25 (AMX system, J_{AM} = 12.5, J_{MX} = 11.0, J_{AX} = 5.5 Hz, 3 H), 1.45 (d, 3 H).

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(11) The exchange of the olefinic ligand should be described by a dissociative process with the intermediate formation of the aryne zirconocene complex **4**. In solution the rapid reverse reaction precludes the direct observation of this process. Under special conditions (vide supra) the thermally induced dissociation of 1-hexene from **12** can indeed be observed.

(12) The rate at the beginning of the reaction (eq 4) can be expressed by $v_0 = k_1[\mathbf{7}]\,(1 + k_{-1}/k_3[\text{norbornene}])^{-1}$; v_0 is independent of the norbornene concentration for $k_{-1} \ll k_3[\text{norbornene}]$.

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Non-Br⁻-Controlled Oscillations in the Belousov–Zhabotinskii Reaction of Malonic Acid

Sir:

The principal features of the chemical mechanism for the temporal oscillations in the Belousov-Zhabotinskii[1-3] reaction have been elucidated by Field, Körös, and Noyes.[4-6] Their mechanism applies a hypothesis originally proposed by Zhabotinskii. According to that supposition in the course of the oscillations, the oxidation of Ce^{3+} by acidic bromate is inhibited periodically by bromide whenever the concentration of bromide exceeds a critical value. That is, in the classical oscillations the bromide ion is a key reference reactant, a control intermediate, the concentration variation of which "turns on" and "turns off" certain chemical processes. In our experiments we could detect oscillations of the redox potential when the bromide concentration was much below its critical value. During these oscillations the potential of a bromide-ion-specific electrode changes monotonically or undergoes very small amplitude oscillations.

The aim of the experiments was to observe the classical BZ system when the natural bromide concentration was depleted

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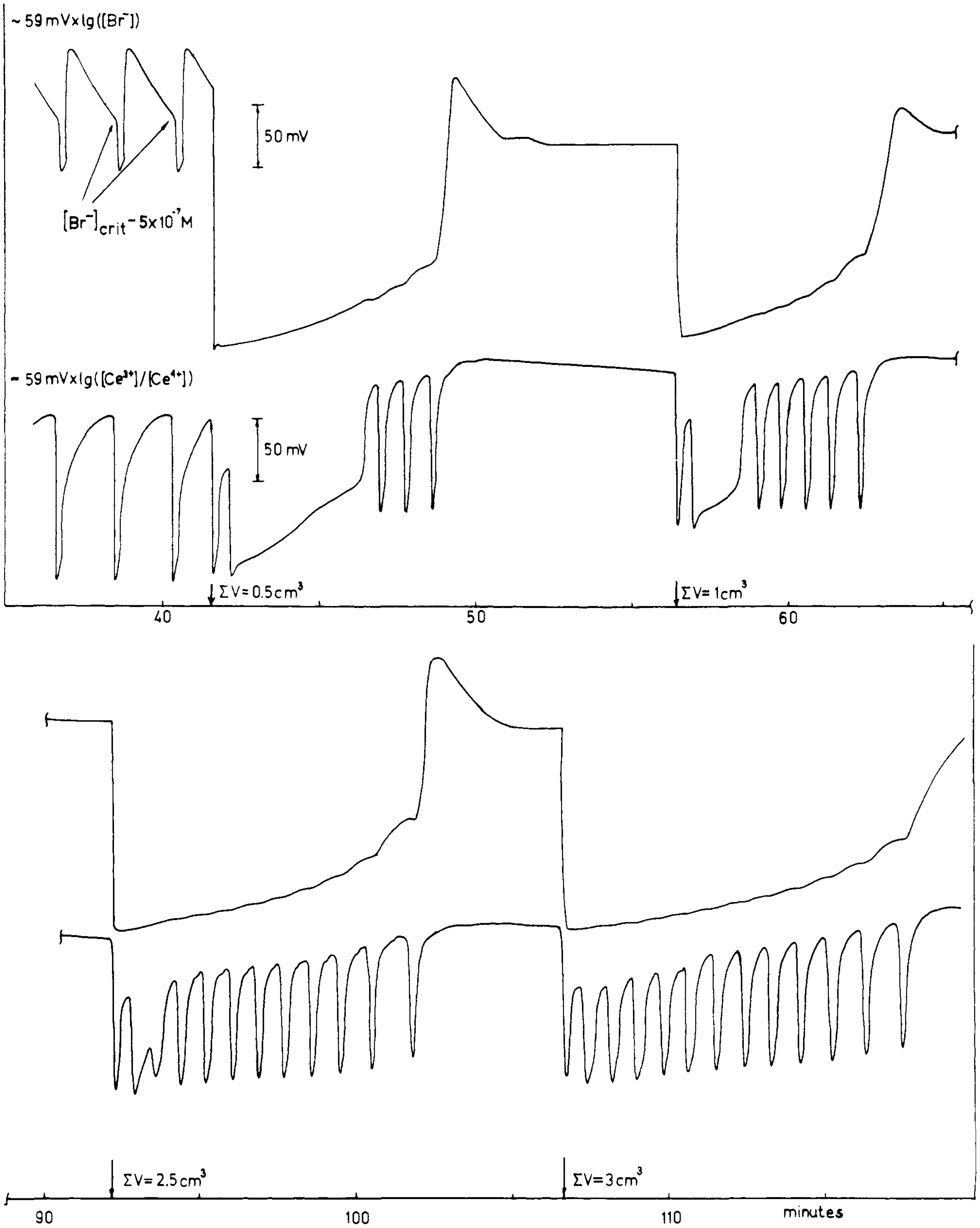

Figure 1. Synchronous potentiometric traces of the Br^- sensitive and the platinum electrode in the classical BZ reaction before and after $AgNO_3$ addition. Initial concentrations: [MA] = 10^{-1} M, [$KBrO_3$] = 4×10^{-2} M, [$Ce(SO_4)_2$] = 10^{-3} M, [H_2SO_4] = 1.5 M. Initial volume: 40 cm^3. At the moments indicated by arrows on the diagram, 0.5 cm^3 of 0.1 M $AgNO_3$ solution was added to the system. A cumulative variable "ΣV" shows the sum of the added volumes.

by silver ions. The bromide concentration was monitored by an ion-selective electrode (Orion Research 94-35). It is often mentioned[4] that in static systems the electrode does not behave ideally in dilute bromide solutions (below 10^{-6} M [Br^-]). This is not a problem here because in our case at lower bromide concentrations the silver ion concentration controls the bromide concentration through the solubility product. To check the electrode in this respect 50 cm^3 of 10^{-3} M bromide solution

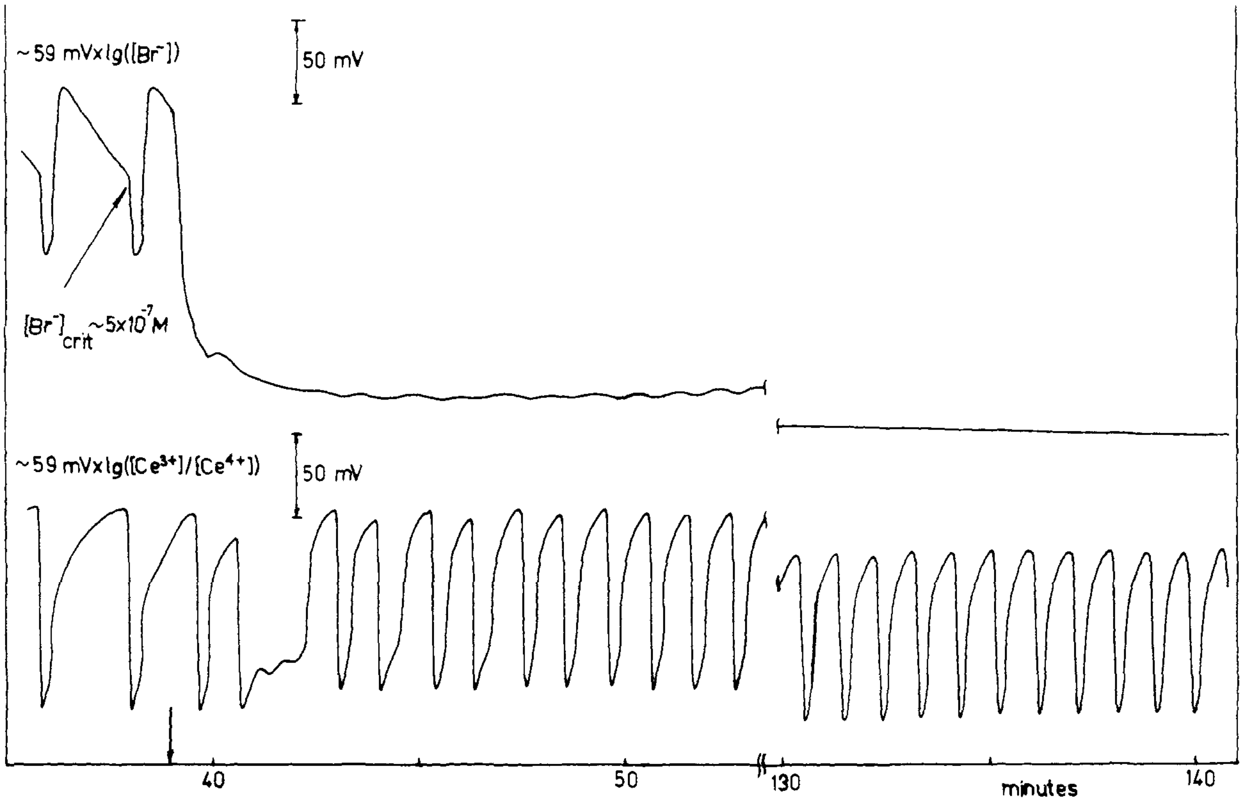

Figure 2. Synchronous potentiometric traces of the Br^- sensitive and the platinum electrode in the classical BZ reaction before and after the continuous Ag^+ production. The initial conditions were the same as indicated in the caption to Figure 1. The electrolyzing current was 5 mA and a current density of 1 mA/cm^2 was applied. The arrow on the diagram indicates the moment when the Ag^+ production was started.

(H_2SO_4 concentration was 1.5 M) was titrated with 1 cm^3 of 10^{-1} M $AgNO_3$ solution. The calculated potential change $\Delta\varphi_c$ was

$$\Delta\varphi_c = 59 \text{ mV} \log \frac{[Br^-]_b}{[Br^-]_a} = 59 \text{ mV} \log \frac{[Br^-]_b[Ag^+]_a}{L} = 363 \text{ mV} \quad (1)$$

where $[Br^-]_b = 10^{-3}$ M, the bromide concentration before the titration; $[Br^-]_a = 7 \times 10^{-10}$ M, the bromide concentration after the titration; and $L = 7 \times 10^{-13}$ M^2, the solubility product of AgBr at 25 °C.[7] The measured value was 350 mV. The redox potential of the system was monitored by a platinum electrode (Radelkis OP-612). The reference electrodes were platinum (Radelkis OP-612) for the redox, and saturated calomel (Radelkis OP-830) for the bromide sensitive electrode connected via a "salt" bridge containing 1.5 M H_2SO_4 solution. The electrode potential was measured by a millivolt meter (Radelkis TR=1456) connected to a dual channel recorder (Yokogawa F-3052) to display the potentiometric traces.

Effect of $AgNO_3$ Addition. In Figure 1 the potential changes of the platinum and the bromide selective electrode are depicted as they were registered in a classical BZ system. After an induction period and 23 normal oscillations, $AgNO_3$ solution was added to the system to lower the bromide concentration level much below the critical value. After a period of transition three oscillations appeared in the redox potential, and during those oscillations there was a monotonic change only in the bromide concentration, still below its critical value. Repeating the experiment, the transition period become shorter and at last disappeared, and more and more oscillations appeared as illustrated in Figure 1. The amplitude of these "abnormal" oscillations was lower (~30% decrease); the frequency was higher (~100% increase) compared to the "normal" ones. The presence of AgBr precipitate disturbed the system when the usual bromide concentration was restored after several oscillations. Another induction period was needed before the normal oscillations could return again (not shown in the figure).

Effect of a Continuous Silver Ion Source. In another experiment a silver electrode as an anode was placed into the classical BZ system after 15 normal oscillations and an electrolyzing current provided by a current generator was turned on (Figure 2). The cathode was platinum electrode connected to the system by a "salt" bridge junction of 1.5 M H_2SO_4 solution. In this manner a constant source of silver ions was set up, and the "abnormal" state of the system was stabilized. In some intervals the average bromide concentration was one-thousanth of the critical one; nevertheless, the "abnormal" oscillations continued undisturbed. In this case the bromide concentration was also oscillating (not monotonically changing as before), but its amplitude was between 5 and 0.5 mV only. That is, while the relative bromide concentration change for normal oscillations is

$$\frac{[Br^-]_{max} - [Br^-]_{min}}{[Br^-]_{min}} \approx 100 \quad (2)$$

the same ratio for "abnormal" oscillations is only 0.25-0.02 (calculated from the Nernst equation). All the experiments were carried out at room temperature (24 ± 2 °C).

A separate manuscript will be prepared discussing the chemical mechanism responsible for the above-mentioned experimental facts.

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Thermal Decomposition of *cis*-Tetrahydropyridazine-*3,4*-d_2. Relative Rates of Rotation, Cleavage, and Closure for Tetramethylene

Sir:

The only 1,4 biradical described by theorists[1] to date is tetramethylene. Despite the fact that substantial experimental work now exists on 1,4-biradical behavior,[3-8] the relative rates of rotation, cleavage, and closure of the parent system are unknown. Substituted tetrahydropyridazines have been shown to be excellent sources for the thermal generation of stereospecifically labeled 1,4 biradicals.[5] Application of this method to the tetramethylene problem provides an opportunity for the *direct* comparison of experiment and theory.

We report the stereospecific synthesis and thermal decomposition in the gas phase (439 °C) of *cis*-tetrahydropyridazine-*3,4*-d_2 (**2**). In addition, we describe the stereospecific syntheses of *cis*- and *trans*-cyclobutane-*1,2*-d_2 (**3** and **4**). Analyses of the cis/trans stereochemistry in the products from the decomposition of **2** allow an experimental determination of the relative rates of rotation, cleavage, and closure for tetramethylene. Moreover, a stereospecific cleavage reaction to ethylene and nitrogen in competition with a 1,4-biradical pathway from the thermal decomposition of tetrahydropyridazine becomes evident.

Synthesis of *cis*-tetrahydropyridazine-*3,4*-d_2 (**2**) was accomplished as shown in Scheme I.[9] For pyrolyses, a solution of **2** in benzene-d_6 was injected into an evacuated Pyrex chamber (439 °C) and the products were collected in a trap at −196 °C.

The ratio of the two ethylenes to cyclobutane was 83:17 from analytical VPC analysis.[10] These products were separated by preparative VPC for infrared analyses of their respective cis/trans-d_2 ratios.[11] The observed *cis/trans*-ethylene-*1,2*-d_2 ratio from the pyrolysis of **2**, obtained by comparison with authentic mixtures,[12] is 80:20.[13]

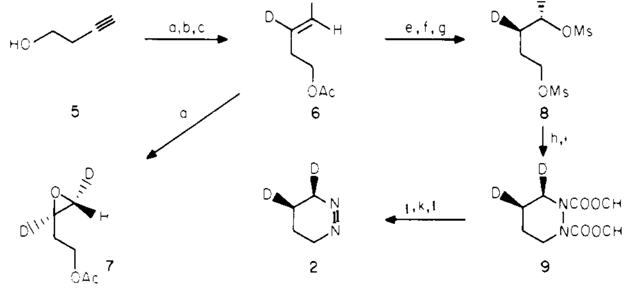
The syntheses of *cis*- and *trans*-cyclobutane-*1,2*-d_2 are shown in Scheme II.[14,15] The ratio of *cis/trans*-cyclobutane-*1,2*-d_2 products from the pyrolysis of **2** was determined by measuring the relative ratio of the 1307 (cis-1,2-d_2) and 1294 cm^{-1} (trans-1,2-d_2) bands in the infrared and comparing these with those of authentic mixtures. The *cis*-tetrahydropyridazine-*3,4*-d_2 (**2**) contains 93% d_2 and 7% d_1. Since cyclobutane-d_1 has a band at 1307, calibration mixtures contained 93% cis,trans-1,2-d_2 and 7% cyclobutane-d_1. The observed *cis/trans*-cyclobutane-*1,2*-d_2 ratio from the pyrolysis of **2** obtained by comparison with authentic mixtures is 56:44.

A summary of the stereochemical results from the thermal decomposition of *cis*-tetrahydropyridazine-*3,4*-d_2 (**2**) is shown in Scheme III.[18] By analogy to previously described decomposition pathways for *cis*- and *trans*-3,4-dimethyltetrahydropyridazines,[5d,e] consider Scheme IV.[19,20]

The ratio of k(cleavage)/k(closure) can be obtained directly. From **2**, the ratio of *crossover* products, *trans*-ethylene-*1,2*-d_2:*trans*-cyclobutane-*1,2*-d_2 is equal to the ratio of the rates for cleavage and closure in the unimolecular decomposition of biradical T. From Scheme III, k_2(closure)/k_3(cleavage) = 7.5:16.6 = 0.45. This k(closure)/k(cleavage) ratio (R_1) and the ratio of *cis-/trans*-cyclobutane-*1,2*-d_2 (R_2) allow a determination of the k(closure)/k(rotation) ratio, k_2/k_1, from a simple steady-state analysis of the proposed diradical scheme, i.e., $k_2/k_1 = (R_2R_1 - R_1)/(R_1 + 1)$. From the data, $R_1 = 0.45$ and $R_2 = 1.27$, we calculate $k_2/k_1 = 0.083$. The experimental ratio of *cis*-ethylene-*1,2*-d_2/*cis*-cyclobutane-*1,2*-d_2 is 66.4:9.52. From k_3/k_2, the amount of *cis*-ethylene-*1,2*-d_2 expected from C should be 2.22 times the *cis*-cyclobutane-*1,2*-d_2 observed (9.52 × 2.22 = 21.1%). Therefore the *extra stereospecific component* of *cis*-ethylene-*1,2*-d_2 is 66.4 − 21.1 = 45.3%.

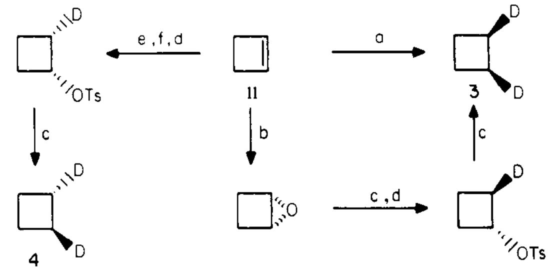
In summary, we find that, in the thermal decomposition of unsubstituted six-membered cyclic 1,2-diazenes at 439 °C in the gas phase, 55% proceeds via tetramethylene, and 45%

Scheme I[a]



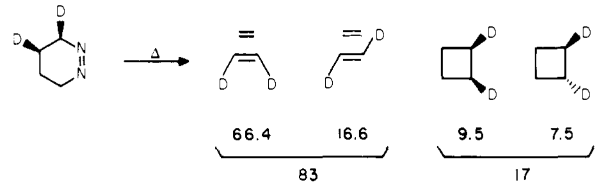
[a] (a) CH_3COCl, (b) $(C_6H_{10}D)_2BD$, (c) CH_3COOD, (d) mCPBA, (e) BH_3, (f) H_2O_2, (g) MsCl, (h) $(HNCOOCH_3)_2/NaH$, (i) NaH, (j) $KOH/H_2O/N_2$, (k) HCl/N_2, (l) O_2/C_6D_6.

Scheme II[a]



[a] (a) N_2D_2, (b) mCPBA, (c) $LiB(C_2H_5)_3D$, (d) TsCl, (e) BD_3, (f) H_2O_2/OH^-.

Scheme III



Scheme IV