The product variation can be consistently interpreted according to the pathways proposed by Savéant and his co-worker[2] that CO_2 reduction involves three competitive pathways: (a) oxalate formation through self-coupling of CO_2^-; (b) formate formation through protonation of CO_2^-; (c) CO formation via oxygen–carbon coupling of CO_2^- with CO_2. The latter two might become prevalent by addition of water or a surfactant to be adsorbed onto the electrode.

By contrast, formate was obtained preferentially in the presence of the clusters even in a dry solution. This supports the view that CO_2^- would be generated through the electron transfer from the reduced clusters to CO_2 in the bulk solution, not on the electrode, and consequently undergo the protonation rather than the self-coupling. The hydrogen atom in the formate produced seems to be derived, at least in part, from tetraalkylammonium ion.[10] In fact, considerable amounts of hydrocarbons consisting mainly of C_3 were detected in the gas analyses after CPE with the clusters. These hydrocarbons were undetectable in such cases where oxalate was predominantly formed.

Works are now in progress to elucidate the reaction mechanism.

Registry No. 1, 52349-82-3; **2**, 52325-39-0; CO_2, 124-38-9; CO, 630-08-0; TBAT, 429-42-5; CTMAT, 73257-08-6; oxalate, 338-70-5; formate, 71-47-6.

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(10) Evidences that tetraethylammonium ion works as proton donor in the reaction with O_2^-, giving rise to ethylene and triethylamine, are provided: Feroci, G.; Roffia, S. *J. Electroanal. Chem.* **1976**, *71*, 191–198.

H/D Secondary Isotope Effects in the Thermal Decomposition of a 1,2-Diaza-1-cyclobutene. Mechanism of Thermolysis

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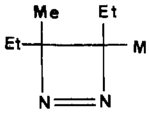
There has been considerable interest for some time in the mechanism of the thermal deazetation of substituted 1,2-diaza-1-cyclobutenes because of the variety of possible decomposition pathways.[1] Aside from a stepwise process involving a biradical-like species residing in a minimum or at the saddle point on the potential surface, synchronous loss of nitrogen by a $[2_s(\text{olefin}) + 2_s(N_2)]$, $[2_a(\text{olefin}) + 2_s(N_2)]$, $[2_s(\text{olefin}) + 2_a(N_2)]$, or $[2_s(\text{olefin}) + \text{"partial"}2_a(N_2)]$ process is conceivable.[1d,2] Studies of the thermal decomposition of *meso-* and *dl*-diazetine **1** excluded the possibility of synchronous loss of N_2 by a concerted $[2_a(\text{olefin}) + 2_s(N_2)]$ process, indicated the unimportance of electronically excited states in this highly exothermic reaction, and placed severe constraints on the lifetime of a diradical derivable by a stepwise cleavage.[1d] In an attempt to learn more about the pyrolytic decomposition of diazetines, we undertook the determination of the α secondary deuterium isotope effects in the previously studied pyrolysis of bicycle **2**, which delivers norbornene and N_2 in a clean reaction.[1a]



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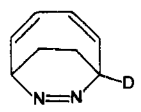

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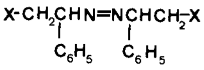

$$X\text{-}CH_2\underset{C_6H_5}{CH}N{=}N\underset{C_6H_5}{CH}CH_2\text{-}X$$

7, X = H
X = C_6H_5
X = C_2H_5
X = OCH_3

Diazetines **2**-d_1 and **2**-d_2, with respectively one and two deuterium atoms in the bridgehead positions α to nitrogen, were synthesized as outlined in Scheme I.[3] Oxidative hydrolysis[4] of adduct **3**[5] results in quantitative conversion to azo-*N*-oxide **4**, which rapidly exchanges the bridgehead proton α to oxidized nitrogen for deuterium in CD_3ONa/CD_3OD at 50 °C to give **5**.[6,7] Reduction with lithium aluminum hydride yielded the diazetine-d_1 **2**-d_1: mp 127–128 °C; λ_{max}(isooctane) 359.1 nm (ϵ 277), 348.6 (273). Saponification of **3** followed by cupric bromide oxidation in situ and decomposition of the resulting metal complex with aqueous ammonium hydroxide led to **2**. The latter readily undergoes H → D exchange at 100 °C in CD_3ONa/CD_3OD at the bridgehead protons α to nitrogen to give diazetine-d_2 **2**-d_2: mp 126.5–127.5 °C, λ_{max}(isooctane) 359.1 nm (ϵ 255), 348.6 (254). NMR analysis gave 95.4 ± 1.4 and 190.0 ± 1.0 atom % of D for **2**-d_1 and **2**-d_2, respectively.[8] The activation parameters for the decomposition of **2** in isooctane are similar to those observed by Lemal et al. in the gas phase ($\Delta H^{\ddagger}_{\text{isooctane}} = 35.3 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger}_{\text{isooctane}} = 6.4 \pm 1.4$ eu; $\Delta H^{\ddagger}_{\text{gas phase}} = 33.7 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger}_{\text{gas phase}} = 3.0 \pm 1.0$ eu).[1a] The isotope effects determined by simultaneously observing the rates of disappearance of **2**, **2**-d_1, and **2**-d_2 at 140.65 °C in isooctane are listed in Table I.[9]

Several groups have reported that the replacement of hydrogen by deuterium on the carbon atom α to nitrogen of an azoalkane increases $\Delta G^{\ddagger}$ when the carbon–nitrogen bond is breaking.[10] For five-membered cyclic azoalkanes (pyrazolines) these effects have

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[*] Present address: The Technological Institute, Gregersensvej, DK-2630 Tåstrup, Denmark.

(1) (a) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5668–5669. (b) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409–1415. (c) Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1876–1882. (d) White, D. K.; Greene, F. D. *Ibid.* **1978**, *100*, 6760–6761. (e) Whitman, D. W.; Carpenter, B. K. *Ibid.* **1980**, *102*, 4272–4274. Wildi, E. A.; Engen, D. V.; Carpenter, B. K. *Ibid.* **1980**, *102*, 7994–7996. (f) Wildi, E. A., Carpenter, B. K. *Tetrahedron Lett.* **1978**, *2469*–2472. (g) Pincock, J. A.; Druet, L. M. *Ibid.* **1980**, *21*, 3251–3252. (h) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092–4093.

(2) In contrast to the cyclobutane → ethylene decomposition, where the $[_\sigma 2_s + {}_\sigma 2_a]$ pathway is allowed, the $[2_s(\text{olefin}) + 2_a(N_2)]$ process is forbidden. Thus the diazacyclobutene σ_-(A), σ_+(S), π_{NN}(A), n_+(S), and n_-(A) orbitals cannot transform into the olefin π_{CC}(S) and nitrogen π_{NN}(S), π_{NN}(A), n_+(S), and n_-(A) orbitals, if orbital symmetry is to be conserved by using a 2-fold axis of symmetry. Since this pathway furthermore involves a very strained transition state, it must be considered less likely than the $[2_s(\text{olefin}) + 2_s(N_2)]$ path.

(3) All new compounds exhibited consistent spectroscopic properties and yielded satisfactory elemental analyses.

(4) Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1524–1536.

(5) Prepared by a [2 + 2 + 2] cycloaddition of MTAD and quadricyclane followed by hydrogenation over palladium–charcoal.

(6) The ^{1}H NMR spectrum of azo-*N*-oxide **4** shows the bridgehead protons α to nitrogen as two multiplets at δ 5.04 and 3.71. The signal at lowest field disappears after treatment with CD_3ONa/CD_3OD.

(7) Attempts to exchange the bridgehead proton α to unoxidized nitrogen at higher temperatures (100 °C) resulted in decomposition.

(8) The NMR measurements involved a minimum of five independent determinations of the proton ratios for labeled and unlabeled compounds by integration following repetitive scanning with a Varian XL-100 spectrometer. The error is given by the standard deviation.

(9) The rate of decomposition was determined by following the disappearance of the absorption at 359.1 nm with a Cary 17 spectrometer. The kinetic experiments were carried out by preparing approximately 0.008 M solutions of the azo compounds **2**, **2**-d_1, and **2**-d_2 in isooctane (Fluka for UV spectroscopy, distilled before use) and syringing 4-mL aliquots into 10-mm quartz cuvettes (carefully base washed before use) equipped with Pyrex necks for sample introduction. The samples were degassed by three freeze–thaw cycles and sealed off under low pressure (10^{-7} torr). The samples were heated at 140.65 ± 0.05 °C over several half-lives (up to 5) and periodically monitored at room temperature after the reaction was quenched by sudden chilling (liquid N_2). Unimolecular rate constants were obtained by least-squares analysis of ln $(A_\infty - A_t)$ vs. time. Correlation coefficients of 0.99998 were routinely obtained. ^{1}H NMR investigations of the decomposition products from **2**-d_1 and **2**-d_2 showed that no deuterium scrambling had taken place.

(10) Scheppele, S. A. *Chem. Rev.* **1972**, *72*, 511–532. Dolenko, A. J.; Buncel, E. In "The Chemistry of the Hydrazo, Azo and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; Vol I, Chapter 17, pp 745–750. For a general treatment of isotope effects see: "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowmann, N. S., Eds.; ACS Monograph 167; Van Nostrand-Reinhold: New York, 1970. For a recent review of isotope effects in pericyclic reactions see: Dolbier, W. R. In "Isotopes in Organic Chemistry"; Buncel, E.; Lee, C. C., Eds.; Elsevier: Amsterdam, 1975; Vol 1, pp 27–59.

0002-7863/82/1504-6836$01.25/0

Scheme I

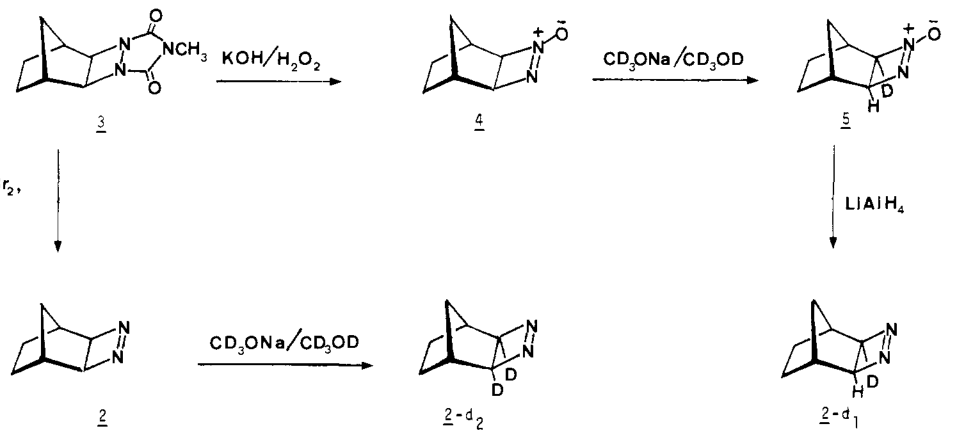

Table I. α-Deuterium Effects in the Thermal Decomposition of Diazetines **2**, **2**-d_1, and **2**-d_2 in Isooctane at 140.65 ± 0.05 °C[a,b]::

run	$(k_2/k_{2\text{-}d_1})_{\text{expt}}$[c]	$(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{expt}}$[c]	$(k_2/k_{2\text{-}d_1})_{\text{corr}}$[c,d]	$(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}}$[c,e]	ξ[f]	$f_{\text{H/D}}{}^1$[g]	$f_{\text{H/D}}{}^2$[h]
1	1.0536	1.0697	1.0564	1.0748	.0171	1.2154	.9343
2	1.0558	1.0713	1.0586	1.0765	.0166	1.2152	.9378
3	1.0554	1.0660	1.0582	1.0707	.0117	1.1865	.9549
4	1.0615	1.0736	1.0647	1.0789	.0132	1.2029	.9549
5	1.0581	1.0745	1.0611	1.0798	.0173	1.2218	.9378
av	1.0569 ± 0.0030	1.0710 ± 0.0034	1.060 ± 0.003	1.076 ± 0.004	0.0153 ± 0.0025	1.2084 ± 0.0140	0.9439 ± 0.0101

[a] Errors are standard deviations. [b] k_2, $k_{2\text{-}d_1}$, and $k_{2\text{-}d_2}$ measured simultaneously in each run. [c] Isotope effects not rounded for computational purposes. [d] $(k_2/k_{2\text{-}d_1})_{\text{expt}}$ corrected to 1 atom of α-d by means of the equation $(k_2/k_{2\text{-}d_1})_{\text{corr}} = a_1[(k_{2\text{-}d_1}/k_2)_{\text{expt}} - (1 - a_1)]^{-1}$, where a_1 = the atom fraction of D (= 0.954), $\langle(k_2/k_{2\text{-}d_1})_{\text{corr}}/(k_2/k_{2\text{-}d_1})_{\text{expt}}\rangle_{\text{av}} = 1.0028$. [e] $(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{expt}}$ corrected by means of the equation $(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}} = a_2{}^2(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{expt}}[a_1 + (1 - a_1)(k_2/k_{2\text{-}d_1})_{\text{corr}} - (1 - a_2)(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{expt}}[2a_2 + (1 - a_2)(k_2/k_{2\text{-}d_1})_{\text{corr}}]]^{-1}$, where $a_1 = 0.954$ and $a_2 = 0.950$, $\langle(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}}/(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{expt}}\rangle_{\text{av}} = 1.0048$. [f] $\xi \equiv 1 - [(k_2/k_{2\text{-}d_1})_{\text{corr}}/(k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}}]$. [g] $f_{\text{H/D}}{}^1 = (k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}}(1 + \xi^{1/2})$. [h] $f_{\text{H/D}}{}^2 = (k_{2\text{-}d_1}/k_{2\text{-}d_2})_{\text{corr}}(1 - \xi^{1/2})$.

been in the range k_H/k_D = 1.10–1.11 (at 140.65 °C), corresponding to $\delta\Delta G^{\ddagger}$ = 77–88 cal/deuterium atom.[11,12] The isotope effects in the decomposition of azocycle **6**[13] and phenylazoalkanes **7** are of the same order of magnitude, i.e., k_H/k_D (**6**) = 1.09[14] and k_H/k_D = 1.08–1.10[15] (at 140.65 °C),[12] corresponding to $\delta\Delta G^{\ddagger}$ = 73.6 and $\delta\Delta G^{\ddagger}$ = 66.6–76.2 cal/deuterium atom, respectively. It is seen from the table that the α effect for **2** is smaller, k_H/k_D = 1.060 ± 0.003, corresponding to $\delta\Delta G^{\ddagger}$ = 47.9 cal/deuterium atom.

Insight into the question of the timing of bond rupture in the deazetation of **2** is gained by the comparison of $k_2/k_{2\text{-}d_1}$ with $k_{2\text{-}d_1}/k_{2\text{-}d_2}$. If the transition state for N_2 loss is symmetrical and provided that the effect of isotopic substitution of one α hydrogen is quantitatively independent of the isotope at the other α position—an approximation pertaining to the rule of the geometric mean, and believed to hold with high accuracy[16a] —then $k_2/k_{2\text{-}d_1}$ should equal $k_{2\text{-}d_1}/k_{2\text{-}d_2}$.[16] In five experiments (table) the values of the former rate constant ratio ranged from 1.054 to 1.0615, those of the latter from 1.066 to 1.074, showing a systematic difference that was slightly enhanced by correction for incomplete deuteration of substrates, the corrected averages being respectively 1.060 ± 0.003 and 1.076 ± 0.004. For the parameter ξ defined as $1 - [(k_2/k_{2\text{-}d_1})/(k_{2\text{-}d_1}/k_{2\text{-}d_2})]$ we find $\xi = 0.015 \pm 0.003$.[17] This result indicates that the decomposition of **2** proceeds by a mechanism involving an unsymmetrical transition state with elementary kinetic isotope effects $f_{\text{H/D}}{}^1 \neq f_{\text{H/D}}{}^2$ for the breaking of individual C–N bonds. Since $k_{2\text{-}d_1}/k_{2\text{-}d_2} = (f_{\text{H/D}}{}^1 + f_{\text{H/D}}{}^2)/2$ and $k_2/k_{2\text{-}d_2} = (k_{2\text{-}d_1}/k_{2\text{-}d_2})(k_2/k_{2\text{-}d_1}) = f_{\text{H/D}}{}^1 f_{\text{H/D}}{}^2$,[16a] $f_{\text{H/D}}{}^1$ and $f_{\text{H/D}}{}^2$ can be estimated by the expression $f_{\text{H/D}}{}^1 f_{\text{H/D}}{}^2 = (k_{2\text{-}d_1}/k_{2\text{-}d_2})(1 \pm \xi^{1/2})$. The resulting values are $f_{\text{H/D}}{}^1 = 1.208 \pm 0.014$ and $f_{\text{H/D}}{}^2 = 0.944 \pm 0.010$.[19] By application of the Streitwieser[20] and Wolfsberg–Stern[21] treatments for secondary isotope effects, the elementary isotope effects estimated for the decomposition of **2** can be interpreted in terms of hybridization changes on going from ground state to transition state. Since the carbon atoms in the diazacyclobutene ring should be hybridized between sp^2 and sp^3, e.g., sp$^{2.x}$,[22] $(k_H/k_D)_\alpha = 1.208$ and $(k_H/k_D)_\beta = 0.944$ indicate changes of hybridization in the respective directions sp$^{2.x} \rightarrow$ sp^2 and sp$^{2.x} \rightarrow$ sp^3. These changes are consistent with a diradical-like transition state, since the carbon atom belonging to the breaking C–N bond should adopt sp^2 hybridization, whereas the carbon atom belonging to the other C–N bond should adopt tetrahedral geometry at the saddle point.[23,24] This conclusion is in accord

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(11) Crawford, R. J.; Cameron, D. M. *Can. J. Chem.* **1967**, *45*, 691–696. Schneider, M. P.; Crawford, R. J. *Ibid.* **1970**, *48*, 628–632. Al-Sader, B. H.; Crawford, R. J. *Ibid.* **1968**, *46*, 3301–3304. Crawford, R. J.; Cameron, D. M.; Tokunaga, H. *Ibid.* **1974**, *52*, 4025–4032. For more recent work of Crawford et al., see: Chang, M. H.; Crawford, R. J. *Ibid.* **1981**, *59*, 2556–2567. Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837–842.

(12) For purposes of comparison the literature values of the α effect have been extrapolated to 140.65 °C on the assumption that A_H/A_D = 1.

(13) Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 285–287.

(14) The isotope effect has been estimated to be k_H/k_D = 1.116 ± 0.013 in isooctane solution at 64.2 °C; Olsen, H., unpublished results.

(15) Scheppele, S. E.; Grizzle, P. L.; Miller, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 6165–6169. Scheppele, S. E.; Rapp, W. H.; Miller, D. W.; Wright, D.; Marriott, T. *Ibid.* **1972**, *94*, 539–544; Scheppele, S. E.; Seltzer, S. *Ibid.* **1968**, *90*, 358–362.

(16) (a) Taagepera, M.; Thornton, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 1168–1177. (b) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 2745–2754.

(17) With the standard deviations of the atom fractions of deuterium in **2**-d_1 and **2**-d_2 taken into account, the error given by the 95% confidence limit of the mean was estimated to be ±0.004. The standard deviation σ_ξ of ξ was calculated by the expression[18] $\sigma_\xi = \pm[(\partial\xi/\partial a_1)^2\sigma_{a_1}{}^2 + (\partial\xi/\partial a_2)^2\sigma_{a_2}{}^2 + 0.0025^2]^{1/2}$, where $\sigma_{a_1} = \pm 0.014$ and $\sigma_{a_2} = \pm 0.010$.

(18) Bevington, P. R. In "Data Reduction and Error Analysis for the Physical Science"; McGraw-Hill: New York, 1969.

(19) The errors given by the 95% confidence limit of the mean were calculated in a similar way as described in ref 17 to be ±0.024 and ±0.017 for $f_{\text{H/D}}{}^1$ and $f_{\text{H/D}}{}^2$, respectively.

(20) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C., Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326–2332.

(21) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225, 325; *J. Chem. Phys.* **1966**, *45*, 2618–2629.

(22) Klansic, L.; Maksić, Z.; Randić, M. *J. Chem. Soc. A* **1966**, 755–757.

with a recent theoretical study of diazetine fragmentation, which reveals that the preferred mechanism is unsymmetrical and involves a diradicaloid with a pair of coupled electrons, one each residing approximately at C and N.[25]

Finally, we note that since the kinetic method employed in this study only produces information about how unequally the two C–N bonds are ruptured in the transition state, the question of the nature of the pathway followed after the saddle point must be regarded as still open.[26]

Acknowledgment. I am grateful to the Danish Natural Science Research Council and to the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung for generous support of the work and to Professors M. G. Ettlinger (University of Copenhagen) and J. F. M. Oth (ETH, Zürich) for valuable suggestions and Dr. N. Bernth (TI, Tåstrup) for helpful discussions.

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(23) Opposing isotope effects have previously been reported for the thermal decomposition of (α-phenylethyl)azomethane. The α effects were interpreted in terms of a two-step cleavage. See: Seltzer, S.; Dunne, F. T. *J. Am. Chem. Soc.* **1965**, *87*, 2628–2635. See also: von Gustorf, E. K.; White, D. V.; Leitich, J.; Henneberg, D. *Tetrahedron Lett.* **1969**, 3113–3116. Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1978** *100*, 2570–2571.

(24) If hyperconjugative effects were operative, the β-isotope effect should be normal ($k_H/k_D > 1$). See, e.g.: DeFrees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 2323–2327.

(25) Crans, D.; Snyder, J. P., private communication. The work is quoted in the recent review of Engel (Engel, P. S. *Chem. Rev.* **1980**, *80*, 113) on the mechanism of the thermal and photochemical decomposition of azoalkanes.

(26) A true intermediate could intervene on the potential surface. Further possibilities are potential surfaces that sustain "twixtyl"[27] and "continuous diradical"[28] species.

(27) Hoffmann, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091–7097.

(28) von Doering, W. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168–1187; **1975**, *97*, 5512–5520.

Small Ring Cyclic Allenes: An ab Initio Study of the Structure of 1,2-Cyclohexadiene

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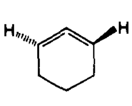
Allenes incorporated in small rings are constrained to bent, near planar geometries.[2] The archetypes of this series, 1,2-cyclohexadiene (**1**) and 1,2-cycloheptadiene were the subjects of recent experimental investigations by Balci and Jones,[3] which provided clear evidence that both are chiral but that **1** racemizes easily, competitive with trapping by cycloaddition with diphenylisobenzofuran. These results seemed to contradict earlier conclusions that 1,2-cyclohexadiene may contain a planar zwitterionic structure such as **3** or **4**.[4-6] Zwitterion **3**, which corresponds to the lowest closed-shell state at this geometry, found support in an INDO study by Dillon and Underwood on C_{2v} planar allene.[6]



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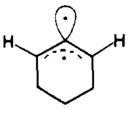

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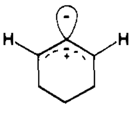

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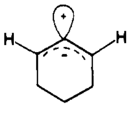

4

We report here results of ab initio MCSCF calculations on 1,2-cyclohexadiene, which support the contention that its equilibrium geometry is strongly bent and chiral (C_2 symmetry) but can easily racemize through a species best described as diradical **2**. Zwitterions **3** and **4** are *electronically excited states* of **2**.[7,8]

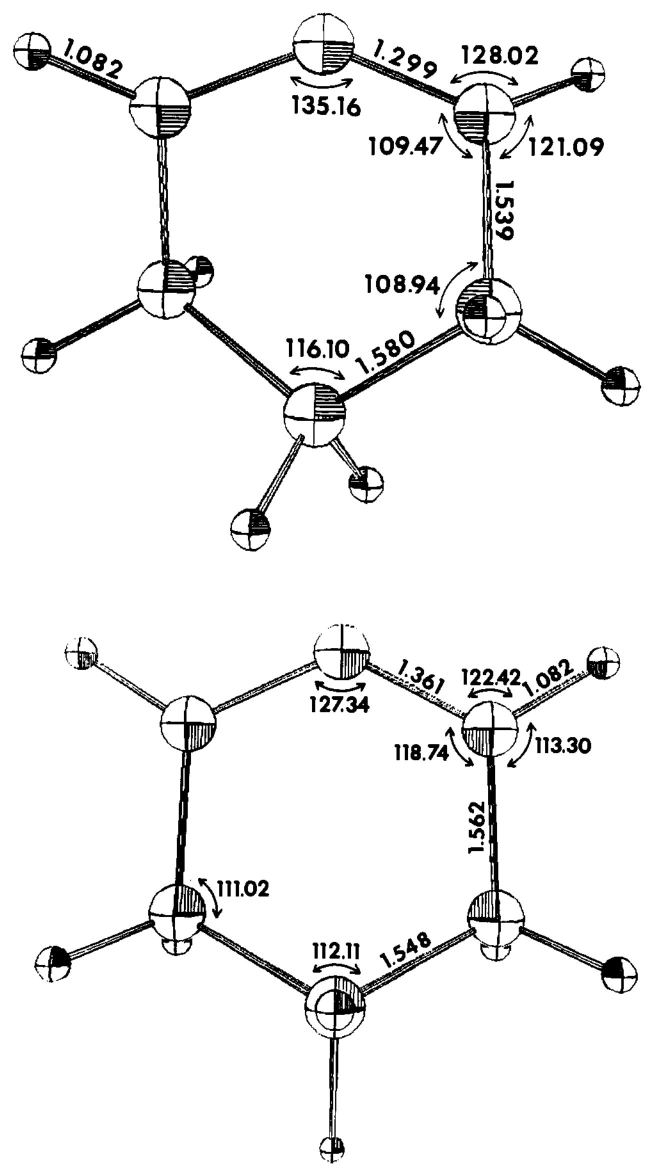

Figure 1. STO-3G geometries for **1** (C_2, top) and **2** (C_s, bottom).

Table I. Computational Results for C_2 and C_s 1,2-Cyclohexadiene[a]

species	state	basis	type	energy	rel energy[b]
1 (C_2)	1^1A	STO-3G	RHF	−228.95597	0.0
		3-21G	RHF	−230.46297	0.0
		3-21G and STO-3G[e]	RHF	−229.74932	0.0
		3-21G and STO-3G[e]	FORS[c]	−229.81769	0.0
2 (C_s)	$1^1A''$	STO-3G	ROHF	−228.96296	−4.4
		3-21G	ROHF	−230.45734	3.5
		3-21G and STO-3G[e]	ROHF	−229.74613	2.0
		3-21G and STO-3G[e]	FORS[d]	−229.79679	13.1
2 (C_s)	$1^3A''$	3-21G and STO-3G[e]	ROHF	−229.74941	
3 (C_s)	$1^1A'$	STO-3G	RHF	−228.79919	

[a] All calculations performed at the STO-3G optimized geometry for the 1^1A or $1^1A''$ states. [b] E(molecule) − E(1) by using comparable basis and level of theory (in kcal/mol). [c] Twelve configuration MCSCF. [d] Eight configuration MCSCF. [e] See footnote 14.

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(1) (a) Iowa State University and Ames Laboratory; (b) Iowa State University.

(2) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

(3) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607.

(4) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469. For recent investigations, see ref 5.

(5) (a) Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* **1975**, *31*, 1997. (b) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Ibid.* **1972**, *28*, 4883.

(6) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779.

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