Reaction of 1 with 2a in Methanol in the Presence of Potassium Hydroxide. 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (7a). A mixture of 1 (11.3 g, 49.7 mmol) and **2a** (5.5 g, 50.4 mmol) containing potassium hydroxide (6 g, 107 mmol) in 150 mL of methanol (absolute or 95%) was refluxed for 3 h with stirring, then poured into water (1200 mL), and neutralized with 2 N HCl. The resulting suspension was extracted with chloroform–acetone (2:1), and the organic phase was dried over anhydrous sodium sulfate and evaporated to dryness. The resulting product was column chromatographed (alumina, neutral V) and eluted with benzene to give **7a** as orange-yellow crystals (chloroform–hexane), 5.59 g (40%), mp 203 °C. It was identical in every respect with an authentic sample of **7a** prepared by another method.

Anal. Calcd for $C_{16}H_8ClNO_2$: C, 68.20; H, 2.86; N, 4.98; Cl, 12.59. Found: C, 68.11; H, 2.90; N, 5.16; Cl, 12.39.

General Procedure for Preparation of Substituted 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-ones (7). A mixture of 1 (2.27 g, 10 mmol), the corresponding substituted *o*-aminophenol **2** (10 mmol), and anhydrous potassium acetate (1.56 g, 20 mmol) in 95% or absolute ethanol or methanol (25 mL or 50 mL) was heated with stirring at 90–100 °C for some hours. The resulting suspension was chilled, filtered, washed with water followed by a little cold ethanol, and dried over phosphorus pentoxide. Repeated recrystallization of the product or column chromatography afforded analytical-grade phenoxazin-5-one. Analytical data, physical constants, solvent of recrystallization, and times of heating of the compounds are collected in Table II.

6,8,9,11-Tetrachloro-5*H*-benzo-[*a*]phenoxazin-5-one (7h). A solution of **2h** (2.01 g, 10 mmol) was prepared in 30 mL of dry chloroform containing triethylamine (5.16 g, 40 mmol) and heated to 50–60 °C for 1 h. To this was added a suspension of 1 (2.27 g, 10 mmol) in 10 mL of dry chloroform over a period of 5 min. After the addition, the reaction mixture was heated to 90–110 °C for 1 h. It was cooled to −2 °C for 5 h. The precipitate was filtered, washed thoroughly with 50% sodium bicarbonate solution and 500 mL of water, and dried to yield light yellow **7h** (3 g, 78%), mp 302 °C, TLC IV. It was identical by IR and mixture melting point with a sample prepared by another method.

5-Acetoxy-6-chloro-12*H*-benzo[*a*]phenoxazine (11). A mixture of **7a** (0.281 g, 1 mmol), acetic anhydride (50 mL) and pyridine (5 mL) was stirred with zinc dust (2 g) for 15 min and then heated on a boiling-water bath for 5 min. The pale yellow solution was separated from the excess zinc dust by filtration and poured into ice for 24 h to yield a light yellow precipitate. This was filtered, washed with water, and dried to yield **11** (0.19 g, 68%), mp 208–210 °C, TLC IV. An analytical sample was obtained by repeated crystallization with benzene–hexane: IR (KBr) 3374 (s, NH), 1748 (s, aromatic acetate) cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 269 (4.39), 319.5 (3.68), 396 (3.68); ^1H NMR (Me_2SO-d_6) 8.41 (s, NH, D_2O exchangeable), 2.49 (s, 3 H), 6.66–8.12 (m, 8 H); mass spectrum, *m/e* (relative intensity) 325 (M^+, 15), 285 (35), 284 (28), 283 (100), 282 (30), 248 (12), 219 (20), 218 (13), 191 (10), 190 (32), 163(9), 162 (9). Anal. Calcd for $C_{18}H_{12}ClNO_3$: C, 66.37; H, 3.71; N, 4.30. Found: C, 65.99; H, 3.61; N, 4.27.

Reaction of 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (7a) with Potassium Hydroxide in Methanol. A solution of **7a** (0.281 g, 0.001 mol) in 30 mL of methanol containing potassium hydroxide (0.04 mol, 2.24 g) was heated with stirring at 90–100 °C for 3 h. The mixture was cooled to room temperature and filtered, and the residue was washed with hexane, dissolved in 200 mL of warm water, filtered, and neutralized with 2 N HCl. The resulting solid was isolated by extraction with chloroform–acetone (1:1) and dried over anhydrous sodium sulfate to give 0.105 g (50%) of 2-chloro-3-hydroxy-1,4-naphthoquinone.[19] An analytical sample was obtained by recrystallization from acetone–hexane, mp 215 °C.

Registry No. 1, 117-80-6; **2a**, 95-55-6; **2b**, 95-84-1; **2c**, 95-85-2; **2d**, 2835-98-5; **2e**, 99-57-0; **2f**, 121-88-0; **2g**, 527-62-8; **2h**, 6358-15-2; **2i**, 4502-10-7; **2j**, 1571-72-8; **4a**, 73396-99-3; **4b**, 73397-00-9; **4c**, 73397-01-0; **5a**, 73397-02-1; **5b**, 73397-03-2; **5c**, 73397-04-3; **5d**, 73397-05-4; **5e**, 73397-06-5; **7a**, 73397-07-6; **7b**, 73397-08-7; [7c], 73397-09-8; **7d**, 73397-10-1; **7e**, 73397-11-2; **7f**, 73397-12-3; **7g**, 73397-13-4; **7h**, 73397-14-5; **7i**, 73397-15-6; **7j**, 73397-16-7; **7k**, 73397-17-8; **7l**, 73397-18-9; **8**, 1916-59-2; **9a**, 258-72-0; **9b**, 1496-98-6; **9c**, 52829-20-6; **11**, 73397-19-0; **12**, 19073-35-9; 3-hydroxy-2-pyridinamine, 16867-03-1; 3-hyroxy-2-naphthalenamine, 5417-63-0; 2-chloro-3-hydroxy-1,4-naphthoquinone, 1526-73-4.

Supplementary Material Available: UV, IR, and mass spectral data for **7a–l** (3 pages). Ordering information is given on any current masthead page.

Ring Expansion Reaction of Cyclopropylcarbene to Cyclobutene[1]

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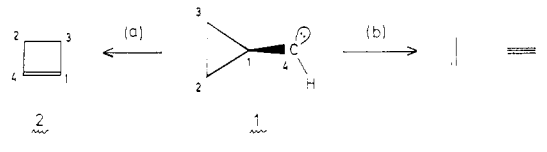
Received February 8, 1980

The ring expansion reaction of cyclopropylcarbene in its singlet ground state $^1(\sigma^2)$ to cyclobutene is initiated by an electrophilic attack of the empty p AO at the carbene site on the most electron-rich carbon atom of the three-membered ring. The reaction is completed by participation of the nucleophilic σ orbital. In the transition state, charge density is accumulated at C_4 and depleted at C_2 and C_1. The stereochemical integrity at the attacked carbon atom is maintained.

Cyclopropylcarbene (1) rearranges thermally[2] primarily to cyclobutene (**2**, route a; see Scheme I), while to a minor

Scheme I



extent the fragmentation to ethylene and acetylene is observed (route b). This side reaction is more probable in the gas phase[3] than in solution. The ring expansion is also stereospecific.[4] When a choice exists, the stronger

(1) Investigations on Carbene Reactions. 4. (a) W. W. Schoeller and U. H. Brinker, *J. Am. Chem. Soc.*, **100**, 6012 (1978); (b) W. W. Schoeller and E. Yurtsever, *ibid.*, **100**, 7548 (1978); (c) W. W. Schoeller, *ibid.*, **101**, 4811 (1979).

(2) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (b) J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965); (c) J. W. Wilt, J. F. Zawadzki, and D. G. Schultenover, S. J., *ibid.*, **31**, 876 (1966); (d) W. Kirmse and K. H. Pook, *Chem. Ber.*, **98**, 4022 (1965); (e) W. Kirmse and K. H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966); (f) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971); (g) D. H. Paskovich and P. W. N. Kwok, *Tetrahedron Lett.*, 2227 (1967); (h) H. M. Ensslin and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **6**, 702 (1967); (i) S. Nishida, I. Moritani, E. Tsuda, and T. Teraij, *Chem. Commun.*, 781 (1969). (j) For further references and a detailed discussion, see "Carbenes", Vol. I, M. Jones, Jr., and R. A. Moss, Eds., Willey, New York, 1973.

(3) P. B. Shevlin and A. P. Wolf, *J. Am. Chem. Soc.*, **88**, 4735 (1966).

(4) (a) A. Guarino and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969); (b) J. A. Berson, W. Bauer, and M. M. Campbell, *J. Am. Chem. Soc.*, **92**, 7515 (1970).

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Table I. Rotational Barrier in Cyclopropylcarbene, Calculated with the MINDO/3, MINDO/2 + 3 × 3 CI, and ab Initio STO-4/31 G Approximations[a,c]

α, deg	MINDO/3	STO-4/31 G	MINDO/2 + 3 × 3 CI		
			$^1(\sigma^2)$	$^1(\sigma^1\rho^1)$	$^3(\sigma^1\rho^1)$
0	0.0	0.0	0.0[b]	19.6	−5.7
30	1.5	3.6	1.0	18.2	−6.2
60	4.3	10.1	3.0	16.1	−7.3
90	4.8	9.7	3.0	17.6	−8.1
120	3.7	4.3	0.6	19.8	−8.2
150	−1.9	0.0	−1.3	18.8	−7.6
180	−3.4	−2.6	−1.9	17.4	−7.1

[a] For an ab initio investigation of the barrier of the corresponding cyclopropylcarbinyl cation, see L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 6380 (1970). [b] Energies are in reference to $^1(\sigma^2)$ with $\alpha = 0°$. [c] Energies are in kilocalories per mole.

bond always migrates.[5] The reaction has been utilized as a route for the general synthesis of substituted cyclobutenes.[6]

No details are yet known for the mechanism of the very common ring expansion reaction of **1** to **2**. In order to reveal a mechanistic concept, we have carried out a quantum mechanical study to determine the electronic hypersurface directing the reaction path.

Methods

We performed calculations at a semiempirical SCF level with the MINDO/3[7] and MINDO/2 + 3 × 3 CI[8] approximations and at an ab initio level with the STO-4/31 G basis set.[9] The geometries calculated with the MINDO/3 method were optimized with respect to the total energy. On this basis, a two-dimensional contour map for the electronic hypersurface was constructed from a series of optimized geometries, each of which was optimized in all degrees of freedom (including bond lengths, bond angles, and torsional angles) until the minimum energy was achieved. For the optimization, a gradient search was employed, the gradient being derived by the method of finite differences.[10]

Results and Discussion

A. Rotational Barrier of Cyclopropylcarbene. In carbene chemistry the following electronic configurations are important:[11] (a) the ground-state singlet $^1(\sigma^2)$, (b) the singly excited singlet $^1(\sigma^1p^1)$, and (c) the triplet $^3(\sigma^1p^1)$. Since **1** corresponds to a substituted methylene, one expects the same order of configurations.[12]

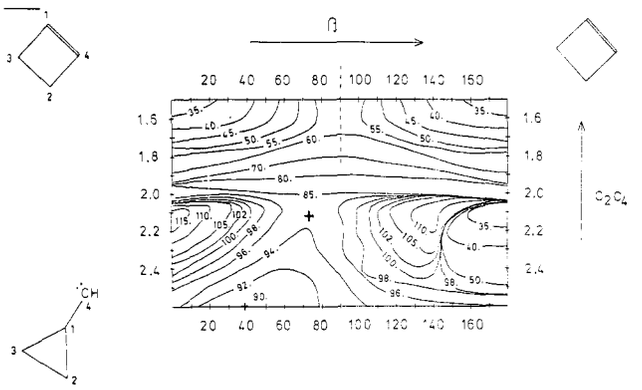
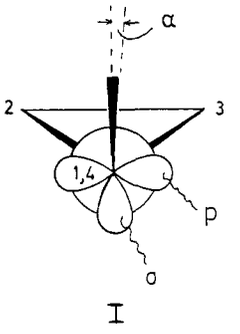


Figure 1. Contour map of the potential energy hypersurface for the ring-expansion reaction from the endo conformation of **1** as a function of the two parameters C_2–C_4 length (in angstrom units) and β (in degrees). The numbers at the contours correspond to heats of formation in kilocalories per mole. The symmetry of the energy contours (70 kcal/mol and below) with respect to the axis of $\beta = 90°$ is due to the occurrence of two enantiomeric structures (see footnote 17). The crosses mark the positions of the educt and the transition state.

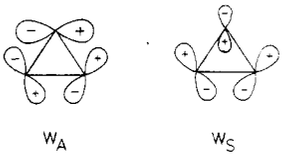
In order to substantiate these arguments the rotational barrier in **1** around the bond C_1–C_4 (see structure I) was



I

calculated by assuming fixed nuclear geometries.[13] The results of these investigations are summarized in Table I.

For the lowest energy singlet $^1(\sigma^2)$, the quantum mechanical procedures predict two energy minima, at $\alpha = 180$ and 0°. The relative stabilities of the different barrier positions can be attributed to two opposing tendencies: (a) the interaction of the empty p AO at C_4 with the antisymmetric component W_A of the set of Walsh orbitals[14]



favors a conformation with $\alpha = 0$ and 180°, respectively; (b) the repulsive interaction[15] of the doubly occupied σ

(5) (a) C. L. Bird, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 707 (1967); (b) I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968).

(6) D. Seebach in "Methoden der Organischen Chemie (Houben-Weyl)", Vol. IV/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1971.

(7) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

(8) (a) W. W. Schoeller, *J. Am. Chem. Soc.*, **97**, 1978 (1975); **99**, 5919 (1977); (b) W. W. Schoeller, *Mol. Phys.*, **37**, 1037 (1979).

(9) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(10) (a) M. J. S. Dewar, H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, and P. K. Weiner, "Quantum Chemistry Program Exchange", program no. 279. An alternative very efficient optimization technique for single-determinant semiempirical wave functions has been reported: (b) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971); (c) A. Komornicki and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **98**, 4553 (1976).

(11) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).

(12) Numerous calculations with increasing accuracy have been reported on the simplest carbene representative, methylene: (a) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972); (b) C. F. Bender, H. F. Schaefer III, D. R. Franzeschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972); (c) V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973); (d) J. H. Meadows and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 4383 (1976); (e) C. W. Bauschlicher, Jr., H. F. Schaefer III, and P. S. Bagus, *ibid.*, **99**, 7106 (1977).

(13) The assumed bonding parameters are as follows: (a) bond lengths, $C_1C_2 = C_1C_3 = C_2C_3 = C_1C_4 = 1.50$ Å, CH = 1.09 Å; (b) bond angles, HCH = 120°, $H_{C_4}C_4C_1 = 120°$, $H_{C_1}C_1C_4 = 120°$. The torsional angle α is defined with respect to a dummy atom bisecting the angle $C_2C_1C_3$.

(14) (a) A. D. Walsh, *Nature (London)*, **159**, 167, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949); (b) T. M. Sugden, *Nature (London)*, **160**, 367 (1947).

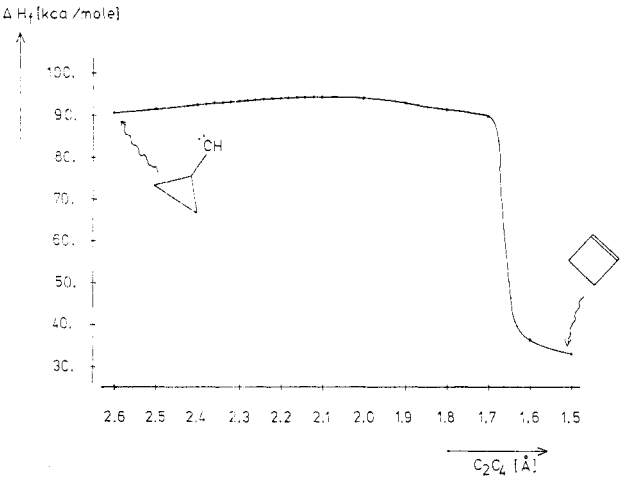
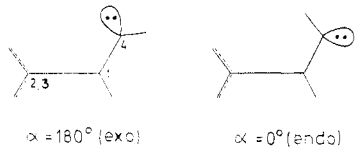


Figure 2. Plot of the calculated heats of formation (in kilocalories per mole) vs. the reaction coordinate (C_2–C_4, in angstrom units) for the MERP of the ring-expansion reaction.

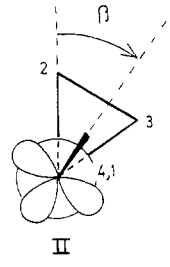
orbital with the symmetric Walsh orbital W_S is less in the exo conformation (α = 180°), due to the smaller overlap of σ with W_S (p AO at C_1).

B. Ring Expansion (Route a). The rearrangement of **1** to **2** involves the formation of a bond between C_2 and C_4 and the breakage of a bond between C_1 and C_2. For this reaction path an electronic hypersurface was computed with the optimized MINDO/3 method, starting from either the exo (α = 180°) or the endo conformation (α = 0°).



Only the investigations for the latter will be summarized in detail here (the pathway for the former is similar). We have restricted our considerations to the singlet state $^1(\sigma^2)$ since this configuration is of most interest to carbene reactions in their singlet ground states.[2j]

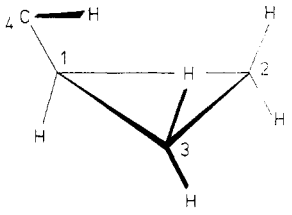
One problem which occurs in the calculations of hypersurfaces for chemical reactions is the proper choice of a reaction coordinate. For the case studied here, a cut through the electronic hypersurface (starting from the endo conformation) is plotted in Figure 1 as a function of two variables, the distance C_2–C_4 and a torsional angle β [=$\angle(H_{C_4}C_4C_1)(C_4C_1C_2)$]. All other bonding parameters, such as bond lengths, bond angles, and torsional angles were optimized with respect to the total energy (heats of formation). A positive value of β corresponds to a right-hand rotation of the hydrogen at C_4 (see structure II).



II

The calculated heats of formation for the minimum energy reaction path (MERP) are recorded in Figure 2, and a corresponding snapshot of the transition state is given in Table II.

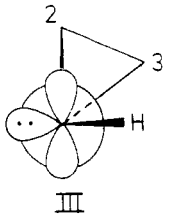
Table II. Molecular Equilibrium Geometries of (1) Cyclopropylcarbene in Its Singlet Ground State, $^1(\sigma^2)$, and of (2) the Transition State Leading from 1 to 2 (Route a) and Starting from the Endo Conformation[a]



parameter	(1)	(2)
C_1-C_2	1.540 (1.540)[b]	1.562 (1.560)[c]
C_1-C_3	1.541 (1.538)	1.509 (1.513)
C_2-C_3	1.459 (1.462)	1.488 (1.478)
C_1-C_4	1.422 (1.423)	1.407 (1.410)
C_2-C_4	2.660 (2.594)	2.120 (2.180)
C_3-C_4	2.681 (2.590)	2.641 (2.579)
HC_2H	108.2 (108.2)	107.3 (107.6)
HC_3H	108.2 (108.1)	107.8 (108.0)
$C_4C_1H_{C_4}$	110.3 (118.7)	117.7 (123.5)
$H_{C_4}C_4C_1$	110.6 (108.9)	112.4 (108.9)
$H_{C_4}C_4C_1C_2$	39.6 (214.7)	73.6 (244.5)

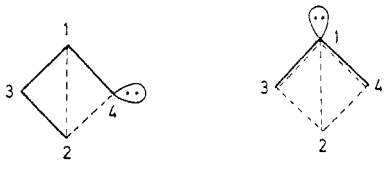
[a] In parentheses are the corresponding bonding parameters for the transition state starting from the exo conformation. Bond lengths are in angstrom units and bond (torsional) angles in degrees. [b] Exo conformation. [c] Transition state from the exo conformation.

The total optimization of **1** in the electronic state $^1(\sigma^2)$ reveals a geometry which is slightly distorted so as to align the empty p AO at C_4 with the bond C_1–C_2. However, the energy difference to the symmetric conformation (β = 30°) of **1** is very small (see Figure 1). In the transition state the bond C_1–C_2 is slightly weakened, while the carbene center forms a weak bond with C_2 (see Figure 1 and Table II). This is also substantiated by an energy-partitioning analysis[16] which will not be recorded here. The hydrogen at C_4 is tilted so as to maximize the overlap of the empty p AO at C_4 with the bonding orbitals at C_2 (see structure III). In this way the closed-shell repulsion of σ with the



III

bonding orbitals at C_2 is avoided. Hence the transition state for the ring expansion reaction is best described by a structure **3**, in which the bonding σ orbital does not



3 4

(15) (a) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968); (b) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955); (c) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968); (d) K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970); (e) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).

(16) (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); (b) W. England and M. S. Gordon, *J. Am. Chem. Soc.*, **93**, 4649 (1971); (c) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970). (d) See ref 8b.

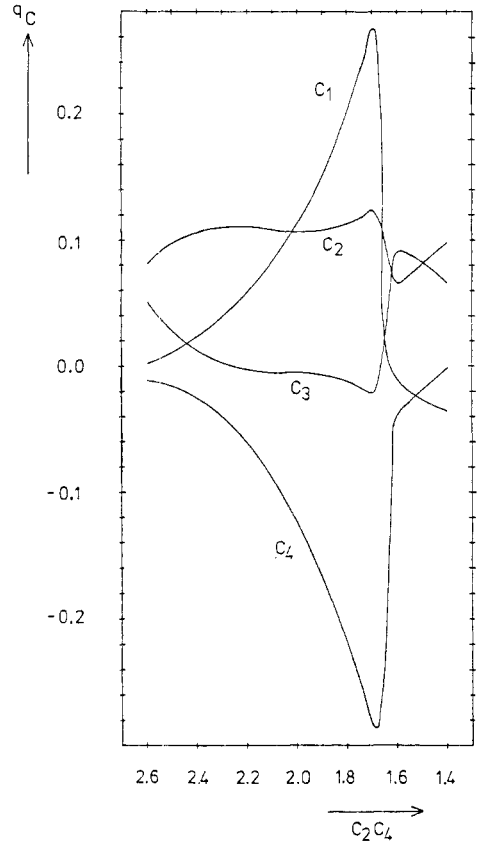
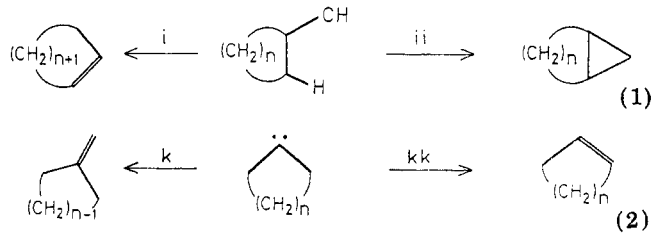


Figure 3. Plot of the charge densities (partial charges) during the course of the reaction from 1 (endo) to **2**.

participate. This is in contrast to the nonclassical carbene structure **4**, an intermediate in the rearrangement of cyclobutanylidene to methylenecyclopropane.[1c] In the latter, electrons from the bonds C_2–C_3 and C_2–C_4 are transferred into the empty p AO at the carbene site C_4.

In proceeding further on the reaction coordinate, the angle β increases steadily until it becomes 180° in the final product cyclobutene. This then corresponds to a completion of the reaction by participation of the σ orbital at the carbene site.[17]

On the basis of the previous findings, one can rationalize the different experimental observations in the ring expansion reaction 1 (eq 1) vs. the ring contraction reaction (eq 2), reported on earlier.[1c] (1) In eq 1 the amount of cyclopropanation product (route ii) increases steadily with increasing[2j] n. This is due to the fact that with increasing n the strain of the C_1–C_2 bond decreases. In other words,



less strain assists the bond breaking of C_1–C_2 less. (2) In eq 2 the contraction reaction (route k) is restricted to the four-membered ring (n = 1). The higher homologues exclusively undergo cycloalkene formation.[1c,2j] This is in accordance with the fact that the intermediate formation of nonclassical species such as **4** is only assisted by *two* strained bonds (C_2–C_3 and C_2–C_4).

The transfer of charge from C_2 into the empty p AO at C_4 is accompanied by a strong polarization in the transition state. A plot of the charge densities throughout the reaction is shown in Figure 3. In the *electrophilic* phase of the reaction, negative charge is built up at C_4 and simultaneously depleted at C_1, and to a minor extent also at C_2. In the *nucleophilic* phase the polarization of the transition state is canceled.

The overall energy barrier (Figure 2) for the expansion reaction amounts to 3.8 kcal/mol, starting from the endo conformation. The transition state from the exo conformation is 1.2 kcal/mol lower in energy. The low overall energy barrier is in accordance with the well-known, experimentally established, easy rearrangement of **1**.

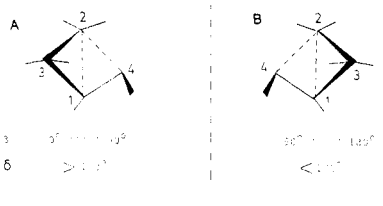
To compute the electronic hypersurface, we used a wave function consisting of a single determinant. Because in the process studied here an *electron pair* is shifted from the bonding orbitals at C_2 toward the empty p AO at C_4, this quantum mechanical treatment should be sufficient. Beyond that, we have checked the influence of configurational interaction. The first order interaction, i.e., inclusion of 3 × 3 CI between the HOMO and LUMO,[8] yields no change of energy, thus corroborating the previous argument.

C. Fragmentation to Ethylene and Acetylene (Route b). According to the pioneering discussion of Woodward and Hoffmann,[18] the fragmentation of **1** into ethylene and acetylene can be classified as a symmetry-allowed process. The orbital correlation is as follows: (a) the Walsh orbital W_S changes into the bonding π MO of ethylene; (b) W_A and σ change into the bonding π MO's of acetylene. Since the retro-Diels–Alder reactions are now well understood,[19] a quantum mechanical study of this side reaction was not attempted.

Conclusions

The results of our investigations can be summarized as follows. (1) The ring contraction reaction (route a) of **1** to **2** is initiated by an electrophilic attack of the empty p AO at the carbene site C_4 on the ring carbon C_2 (C_3). In the transition state, charge is transferred from C_2 (or C_3) into the p AO at C_4. (2) On this basis the transition state should be stabilized by introduction of electron-releasing

(17) With decreasing distance C_2–C_4, the energy contours become symmetric with respect to an axis at β = 90° (dotted line in Figure 1). This corresponds to the appearance of two enantiomeric structures depicted as A and B. Within the same coordinate system the two diastereomers differ in their parameters for β and δ (=$H_{C_4}C_4C_1$). They are either defined by 90° < β > 180°, δ < 180°, or by 0° < β > 90°, δ > 180°. These optical isomers are easily interconvertible since the C_1–C_2 bond becomes weakened with decreasing C_2–C_4 distance. On this basis the formation of a highly strained trans double bond in cyclobutene can be avoided which otherwise would be formed for β = 0°.



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substituents at the ring carbon C_2 (C_3) and at C_1. This corresponds to the migration of the more electron-rich carbon–carbon bond.[5] (3) The ease of rearrangement (low-energy barrier) depends on a three-center bonding between the atoms C_1, C_2, and C_4 and involves two electrons (of the σ bond C_1–C_2). Hence it can be related to the rearrangement of the cyclopropylcarbinyl cation (unpublished results). The stereochemical integrity of the attacked carbon atom C_2 (or C_3) is conserved, and the neighboring carbon atom C_3 (or C_2, respectively) is not affected by the electrophilic attack.

Finally it must be noted that semiempirical SCF methods such as the MINDO procedure are parametrized to reproduce ground-state properties. Hence the criticism which can be applied to the NDO approximation holds.[20] On this basis one may question the numerical accuracy predicated in our study. Only in one case have rigorous good quality ab initio calculations been reported[21] which confirm the results of the semiempirical quantum mechanical investigations.

Acknowledgment. This work was supported by a grant from Land Nordrhein-Westfalen and by the Fond der Chemie. Computer time was generously provided by the Rechenzentrum der Universität Bielefeld.

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Reductive Ring Contraction of Mesoionic Thiazol-4-ones to Azetidin-2-ones

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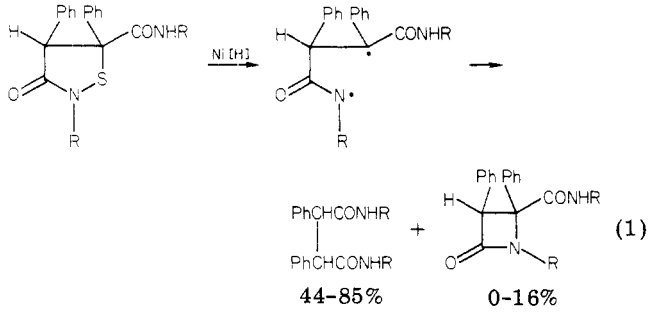
Received December 4, 1979

A series of anhydro-2,3,5-triaryl-4-hydroxythiazolium hydroxides was prepared and desulfurized with Raney nickel. The reduction was stereospecific and gave *cis*-1,3,4-triphenylazetidin-2-ones. Desulfurization in the presence of triphenylphosphine gave the corresponding *trans*-azetidinones. Consideration of the possible mechanistic pathways led to the conclusion that the reaction proceeds through formation of a biradical–dipole, hydrogenation to a 1,4-dipole, and ring closure. It was also concluded that in the preparation of β-lactams by the nonconcerted [2 + 2] cycloaddition of imines and ketenes the first step (dipole formation) is the stereochemistry-determining step.

Among the large number of existing synthetic approaches to the β-lactam system[1] only a few are based on ring contractions.[2] The only reported[3] example which involved Raney nickel desulfurization (eq 1) gave β-lactams in low yields, since the initially generated biradical undergoes hydrogenation rather than internal coupling.[4]

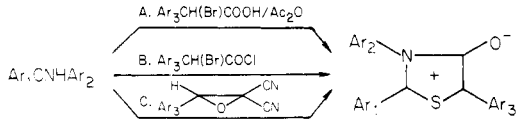


(1)

We expected that the use of mesoionic substrates[5,6] would offer considerable improvement. These compounds, which cannot be formulated by covalent structure, can be expected to furnish dipolar intermediates capable of cyclization even under the reductive desulfurization conditions.

Results[7]

This paper deals mainly with desulfurizations of anhydro-4-hydroxy-2,3,5-triarylthiazolium hydroxides (1). These are prepared by the reaction of thiobenzanilides with either α-bromoarylacetic acids and acetic anhydride[8] (A), α-bromoarylacetyl chlorides[9] (B), or *gem* dicyanoaryl epoxides[10] (C). Compounds 1 prepared for this study and



their physical properties are listed in Table I.

Desulfurization of 1a–j. Treatment of **1a** with Raney nickel (tenfold excess) in methanol, ethanol, tetrahydrofuran, or acetone caused disappearance of its red color within a few minutes. Workup afforded a single product which was identified[11] as *cis*-1,3,5-triphenylazetidin-2-one (**2a**, 85% yield). **1b–j** reacted similarly, yielding the *cis*-azetidinones **2b–j**, respectively (Table II). The yields listed in Table II were obtained under the standard conditions (see Experimental Section) and were rather low in several cases. This is due mainly to hydrogenolytic

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