Molecular Mechanics Calculations of Epoxides. Extension of the MM2 Force Field

Brent L. Podlogar and Douglas J. Raber*

Department of Chemistry, University of South Florida, Tampa, Florida 33620-5250

Received March 1, 1989

Allinger's MM2 force field has been extended to include epoxides. Structural parameters were obtained by determining values that gave best agreement between the calculated and microwave structures of oxirane and 2-methyloxirane. The parameters were then tested with a series of additional epoxides for which previously reported structures had been determined by microwave spectroscopy and X-ray crystallography. Good agreement was found in the comparison of calculated and experimental structures. Calculated heats of formation show qualitatively good agreement for the limited number of available values in the literature.

Introduction

Epoxides have become important compounds in the field of synthetic organic chemistry, and recent advances have provided the methodology to both synthesize and transform epoxides with high stereochemical and regiochemical selectivity.[1] The importance of epoxides as synthetic intermediates has prompted the need for a better understanding of the mechanisms underlying these selectivities. To that end, an accurate computational model for epoxides would be valuable, but to date a general force field for epoxides has not been reported. We have therefore undertaken a study aimed at extending Allinger's MM2 force field[2] to include a variety of substituted epoxides, and the results of this investigation are reported here.

Methods

All calculations were performed on an IBM 3081D utilizing our MM2MX program,[3] which is a modification of Allinger's MM2 program that permits calculations of metal complexes and includes the RIPS algorithm[4] for stochastic searching of conformational space. For routine calculations of organic molecules the MM2MX program is identical to the original MM2 program.[2b]

In order to develop an MM2 force field for epoxides that is as complete as possible, we set about deriving parameters to accurately reproduce experimentally derived structures, dipole moments, and heats of formation. As an initial source for the structural parameters, we considered treating the epoxide carbon as equivalent to a cyclopropane carbon, based on the approximation that a saturated three-membered ring carbon atom would be comparable for both cyclopropanes and oxiranes. This offered the simplification that fewer new parameters would be required, but it quickly became apparent that even the carbon–carbon bond lengths of these two ring systems were sufficiently different (cyclopropane, 1.51 Å; oxirane, 1.47 Å) that the same atom type could not be employed for the carbon in both cases. Consequently, new atom types were defined for both the oxygen, (EO, type 49) and carbon (EC, type 50) of an epoxide ring.

Table I. Stretching Parameters, Bond Moments, and Bond Enthalpies for Epoxides

bond type[a]	k_s, mdyn/Å	l_0, Å	moment, D	bond enthalpy, kcal/mol
1–50	4.400[b]	1.505[b]	0.286	−3.96
2–50	4.400[b]	1.436	*c*	*c*
5–50	4.600[b]	1.0868	0.000[b]	−3.205[b]
20–49	4.600[b]	0.600[b]	−0.900[b]	*d*
49–50	5.360[e]	1.435	−0.735	−25.955
50–50	4.400[b]	1.467	0.000[b]	−7.429$_b$

[a] Epoxide oxygen is assigned 49 and the carbon, 50. [b] Equal to corresponding value for cyclopropane carbon or ether oxygen. [c] Not applicable, parameters for aromatics are not included in MM2. [d] Not applicable, substituent is lone pair of electrons. [e] Value from ref 5.

The development of empirical force field parameters is necessarily an iterative process, and initial structural values were obtained in the following way. Wherever possible, stretching, bending, and torsion parameters were taken from Allinger's current MM2 parameter list[2c] by directly substituting the cyclopropane carbon (type 22) and ether oxygen (type 6) parameters for the epoxide carbon and epoxide oxygen, respectively. The few torsion and bending parameters that could not be derived in this fashion were taken from a list compiled by B. D. Silverman[5] for aromatic epoxides or were approximated with existing MM2 parameters for analogous atom types.

Once a complete set of initial parameters had been obtained in this manner, we proceeded to refine them in order to minimize the differences between calculated structural data and experimental results; adjustments to values of l_0 were adequate for this purpose. Relatively few detailed structural analyses have been reported for epoxides, but the availability of two independent microwave structures for both oxirane (**1**)[6,7] and 2-methyloxirane (**2**)[8,9] provided the experimental references for our parameters. Because MM2 was designed to reproduce bond lengths (r_g) derived from electron diffraction, ad hoc corrections of 0.004 and 0.007 Å were added to the bond lengths of the experimentally derived microwave and X-ray structures, respectively.[10] Oxirane and 2-methyloxirane do not provide sufficient information for evaluation of torsional constants; the initial values corresponding to cyclopropane carbon and ether oxygen were not refined further. The bond dipoles for the carbon–oxygen of the epoxide ring and for the carbon–carbon bond of substituents on the ring

---

[1] (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *102*, 5974. (b) Carlier, P. R.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 2978. (c) Behrens, C.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67.

[2] (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yu, Y, H. *QCPE* **1981**, *13*, 395. (c) Parameter list from MM2 (87), Molecular Design, Ltd., San Leandro, CA; available to academic users as QCPE 543.

[3] Brecknell, D. J.; Ferguson, D. M.; Raber, D. J. *J. Mol. Struct. (Theochem)* **1985**, *124*, 343.

[4] Ferguson, D. M.; Raber, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 4371.

[5] (a) Silverman, B. D. *Cancer Biochem. Biophys.* **1983**, *6*, 131. (b) Silverman, B. D., personal communication.

[6] Hirose, C. *Bull. Chem. Soc. Jpn.* **1974**, *47*(6), 1311.

[7] Turner, T. E.; Howe, J. A. *J. Chem. Phys.* **1956**, *42*, 924.

[8] Swalen, J. D.; Herschbach, D. R. *J. Chem. Phys.* **1957**, *27*, 100.

[9] Creswell, R. A.; Schwendeman, R. H. *J. Mol. Spectrosc.* **1977**, *64*, 295.

[10] Allinger, N. L. Brief Guidelines for Obtaining Parameters for the MM2 System *QCPE* **1988**, (8).

0022-3263/89/1954-5032$01.50/0

Table II. Bending Parameters for Simple Epoxides

angle type	k_b, mdyn/Å rad^2	θ_0, deg
1–1–50	0.450	112.400
1–50–49[a]	0.560	115.000
1–50–1	0.450	120.000
1–50–2[b]	0.450	120.000
1–50–5	0.360	123.500
1–50–50	0.600	118.200
2–1–50	0.450	112.400
2–2–50	0.550	121.000
2–50–49[a]	0.560	115.000
2–50–50	0.600	118.200
5–1–50	0.360	109.410
5–50–5	0.320	120.600
5–50–49[a]	0.430	113.000
5–50–50	0.360	124.500
20–49–20	0.240	131.000
20–49–50[c]	0.350	103.000
49–50–50[a]	0.560	59.300
50–49–50[a]	0.620	61.400

[a] Value from ref 5. [b] Approximated with a type (2–22–2) or a type (1–22–1), ref 2. [c] Approximated with a type (2–6–20), ref 2.

Table III. Torsional Parameters for Simple Epoxides[a,b]

dihedral angle type	V_1	V_2	V_3
1–1–1–50	0.200	−0.200	0.600
1–1–50–1	0.000	0.000	0.000
1–1–50–2[c]	0.000	0.000	0.000
1–1–50–5	0.000	0.000	0.267
1–1–50–49[d]	0.000	0.000	0.530
1–1–50–50	0.300	0.000	0.450
1–2–2–50[d]	−1.140	16.250	0.000
1–50–1–5	0.000	0.000	0.690
1–50–2–2[e]	0.100	0.000	0.500
1–50–49–20[f]	0.000	0.000	0.000
1–50–49–50[d]	0.000	0.000	1.210
1–50–50–1	0.200	0.270	0.093
1–50–50–2[g]	0.200	0.270	0.093
1–50–50–5	0.000	0.000	0.120
1–50–50–49[d]	0.000	0.000	0.530
2–1–1–50[d]	0.000	0.000	0.530
2–2–2–50	−0.270	15.000	0.000
2–2–50–49[d]	0.000	0.000	0.000
2–2–50–50	−0.440	0.240	0.060
2–50–49–50[d]	0.000	0.000	1.210
2–50–50–5	0.000	0.000	0.120
2–50–50–49[d]	0.000	0.000	0.530
5–1–1–50	0.000	0.000	0.167
5–1–50–5	0.000	0.000	0.690
5–1–50–2[h]	0.000	0.000	0.690
5–1–50–49[d]	0.000	0.000	0.530
5–1–50–50	0.000	0.000	0.120
5–2–1–50	0.000	0.000	0.010
5–2–2–50	0.000	15.000	0.000
5–50–49–20[f]	0.000	0.000	0.000
5–50–49–50[d]	0.000	0.000	1.210
5–50–50–5	0.000	0.000	0.137
5–50–50–49[d]	0.000	0.000	0.530
20–49–50–2[f]	0.000	0.000	0.000
20–49–50–50[f]	0.000	0.000	0.000

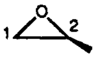
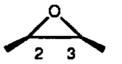
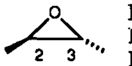
[a] Values correspond to current MM2 parameters for cyclopropane carbon and ether oxygen unless otherwise indicated; see text. [b] Threefold torsional constants in kilocalories/mole. [c] Approximated with type (1–1–22–1), ref 2. [d] Values from ref 5. [e] Estimated from type (2–2–22–2), ref 2. [f] All torsional parameters which include a type 20 atom (lone pair) have been set to $V_1 = 0$, $V_2 = 0$, and $V_3 = 0$ in accord with all others in ref 2. [g] Estimated from type (2–22–22–2) or (1–22–22–1), ref 2. [h] Estimated from type (5–1–22–1) or (5–1–22–5), ref 2.

Table IV. VDW Parameters for Simple Epoxides[a]

atom type	ε, kcal/mol	radius, Å
49	0.050	1.74
50	0.044	1.90

[a] Values equal to those for ether oxygen (type 6) and cyclopropane carbon (type 22), respectively.

Table V. Comparison of Calculated and Microwave Structures[a]

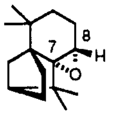
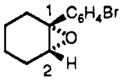
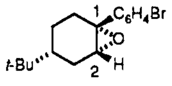
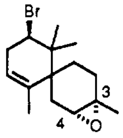
compound	structure feature	experimental[b]	calculated	exp – calc
oxirane (1)[c]				
	EC–EC	1.474 (0.003)	1.474	0.000
	EC–H	1.089 (0.004)	1.089	0.000
	EC–EO	1.438 (0.002)	1.439	−0.001
	EC–EC–EO	59.20	59.20	0.00
	EC–EO–EC	61.64	61.60	0.04
	dipole moment	1.88 (0.01)[d]	1.89	−0.01
oxirane (1)[e]				
	EC–EC	1.474 (0.001)		0.000
	EC–H	1.087 (0.002)		−0.002
	EC–EO	1.439 (0.001)		0.000
	EC–EC–EO	59.09		−0.11
	EC–EO–EC	61.81		0.21
2-methyloxirane (2)[f]				
	EC(1)–EC(2)	1.475	1.476	−0.001
	EC(1)–EO	1.440	1.440	0.000
	EC(2)–EO	1.440	1.439	0.001
	C(2)–C(4)	1.517 (0.02)	1.516	0.001
	EC(1)–EC-(2)–EO	59.19	59.18	0.01
	EC(2)–EC-(1)–EO	59.19	59.13	0.00
	EC–EO–EC	61.61	61.68	−0.07
	dipole moment	2.00 (0.02)	1.97	0.03
2-methyloxirane (2)[g]				
	EC(1)–EC(2)	1.468 (0.02)		−0.008
	EC(1)–EO	1.451 (0.02)		0.011
	EC(2)–EO	1.454 (0.02)		0.015
	C(2)–C(4)	1.503 (0.01)		−0.013
	EC(1)–EC-(2)–EO	59.4 (0.5)		0.2
	EC(2)–EC-(1)–EO	60.2 (0.8)		1.1
	EC–EO–EC	60.4 (0.7)		−1.3
cis-2,3-dimethyloxirane (3)[h]				
	EC–EC	1.475	1.482	−0.007
	EC–EO	1.440	1.440	0.000
	EC–H	1.086	1.091	−0.005
	EC–C	1.517 (0.02)	1.519	−0.002
	EC–EC–EO	59.19	59.03	0.16
	EC–EO–EC	61.61	61.93	−0.32
	dipole moment	2.01 (0.02)	2.04	−0.03
trans-2,3-dimethyloxirane (4)[i]				
	EC–EC	1.475	1.478	−0.003
	EC–EO	1.440	1.439	0.001
	EC–H	1.086	1.091	−0.005
	EC–C	1.517 (0.02)	1.517	0.000
	EC–EC–EO	59.19	59.10	0.09
	EC–EO–EC	61.61	61.80	−0.19
	dipole moment	2.03 (0.04)	2.01	0.02

[a] Dipole moments (Debyes) from microwave data; bond lengths in angstroms; bond angles in degrees. [b] All experimental bond lengths have been adjusted to r_g by adding 0.004 Å to the reported values; experimental errors in parentheses. [c] Reference 6. [d] Reference 11. [e] Reference 7. [f] Reference 8. [g] Reference 9. [h] Reference 12. [i] Reference 13.

were calculated to best reproduce the dipole moments of 1–4.[8,11–13]

After the structural parameters had been partially refined, we turned to heat of formation parameters, i.e., bond enthalpies. The corresponding cyclopropane parameters were again employed in the first iteration, and these values were first adjusted according to the premise that any discrepancy could be attributed entirely to the carbon–oxygen (EC–EO) bond enthalpies of the epoxide ring. After first adjusting this value to exactly reproduce the

Table VI. Comparison of Calculated and Crystal Structure Results

compound	structure feature	experimental[a]	calculated	exp - calc
epoxyisolongefolene (**5**)[b]				
	EC-EC	1.461 (4)	1.480	-0.019
	EC(7)-EO	1.452 (3)	1.434	0.018
	EC(8)-EO	1.456 (4)	1.440	0.016
	EC(8)-EC(7)-EO	60.0	59.2	0.8
	EC(7)-EC(8)-EO	59.6	58.8	0.8
	EC-EO-EC	60.4	62.0	-1.6
1-(*p*-bromophenyl)-1,2-epoxycyclohexane (**6**)[c]				
	EC-EC	1.478 (0.02)	1.483	-0.005
	EC(1)-EO	1.452 (0.02)	1.436	0.016
	EC(2)-EO	1.476 (0.02)	1.442	0.034
	EC(2)-EC(1)-EO	60.5 (1.0)	59.2	1.3
	EC(1)-EC(2)-EO	58.9 (1.0)	58.8	0.1
	EC-EO-EC	60.6 (1.0)	62.0	-1.4
trans-4-*tert*-butyl-1-phenyl-1,2-epoxycyclohexane (**7**)[d]				
	EC-EC	1.485 (3)	1.478	0.007
	EC(1)-EO	1.473 (3)	1.432	0.041
	EC(2)-EO	1.455 (3)	1.439	0.016
	EC(2)-EC(1)-EO	58.9 (2)	58.8	0.1
	EC(1)-EC(2)-EO	60.2 (2)	59.2	1.0
	EC-EO-EC	60.9 (2)	62.0	-1.1
chamigrene epoxide (**8**)[e]				
	EC-EC	1.475 (9)	1.472	0.003
	EC(3)-EO	1.469 (9)	1.437	0.032
	EC(4)-EO	1.473 (8)	1.440	0.033
	EC(3)-EC(4)-EO	59.7	59.2	0.5
	EC(4)-EC(3)-EO	60.1	59.3	0.8
	EC-EO-EC	60.2	61.5	-1.3

[a] All experimental bond lengths have been adjusted to r_g by adding 0.007 Å to the reported X-ray values; estimated standard deviations in parentheses. [b] Reference 14. [c] Reference 15. [d] Reference 16. [e] Reference 17.

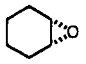
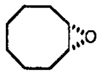
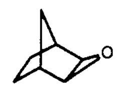
heat of formation of **1**, a slight adjustment to the $EC-CH_3$ bond enthalpy (from -2.333 to the present value of -3.96) was applied to optimize the agreement between calculated and experimental heat of formation for **2**.

Results and Discussion

The epoxide structural parameters were obtained by optimizing the fit between calculated and experimental structures for oxirane (**1**) and 2-methyloxirane (**2**), and the parameters are listed in Tables I-IV. A comparison of calcualted vs microwave structures is summarized in Table V for the two epoxides used in the parameterization together with the analogous results for *cis*-2,3-dimethyloxirane (**3**) and *trans*-2,3-dimethyloxirane (**4**). Bond lengths and angles involving the epoxide ring are generally reproduced to within 0.01 Å and 0.1°, respectively. The largest discrepancies between calculated and experimental values also correspond to significant disagreements between two microwave values. Note that the microwave studies themselves are not fully independent, the same ring angles being assumed for the two stereoisomeric dimethyloxiranes[12,13] as for 2-methyloxirane.[8] Calculated dipole moments also agree well with experimental values[8,11-13] for the compounds investigated.

The parameter set was next tested by calculating structures for a series of epoxides (**5**-**8**) for which structures had been determined by X-ray crystallography.[14-17] The results are summarized in Table VI. Although X-ray structures are generally considered to be less reliable than microwave or electron diffraction structures because of their sensitivity to thermally induced vibrations,[18] we still find excellent agreement with our calculated structures.

Table VII. Comparison of Calculated and Experimental Heats of Formation (kcal/mol)

compound	experimental[a]	calculated	exp - calc
 oxirane (**1**)[b]	-12.58 (0.15)	-12.58	0.00
 2-methyloxirane (**2**)[c]	-22.63	-22.63	-0.00
 cyclohexene oxide (**9**)[d]	-30.46 (0.279)	-32.96	2.50
 cyclooctene oxide (**10**)[d]	-39.45 (0.581)	-37.75	-1.70
 norbornene oxide (**11**)[d]	-12.59 (0.64)	-12.58	-0.01

[a] Values in parentheses represent reported experimental error. [b] Reference 19. [c] Reference 20. [d] Reference 21.

The heat of formation results, reported in Table VII, were derived entirely from compounds **1** and **2**, for which perfect agreement between experiment[19,20] and calculation is found. Compounds **9**-**11** exhibit larger differences between calculated and experimental[21] values. The structural

---

(11) McClellan, A. L. In *Tables of Experimental Dipole Moments*; W. H. Freeman & Co.: San Francisco, CA, 1963; p 65.

(12) Sage, M. L. *J. Chem. Phys.* **1961**, *35*, 142.

(13) Emptage, M. R. *J. Chem. Phys.* **1967**, *47*, 1293.

(14) McMillan, J.; Paul, I. *Tetrahedron Lett.* **1974**, 419.

(15) Merlino, S.; Lami, G.; Macchia, B.; Monti, L. *J. Org. Chem.* **1972**, *37*, 703.

(16) Domiano, P.; Macchia, F. *Acta Crystallogr.* **1980**, *B36*, 3067.

(17) Suzuki, M.; Furusaki, A.; Kurosawa, E. *Tetrahedron* **1979**, *35*, 823.

(18) Burkert, U.; Allinger, N. L. In *Molecular Mechanics, ASC Monograph 177*; American Chemical Society: Washington, DC, 1982.

(19) Cox, J. D.; Pilcher, G. In *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(20) Oetting, F. L. *J. Chem. Phys.* **1964**, *41*, 149.

Table VIII. Summary of MM2 Calculated Steric Energies and Heats of Formation (kcal/mol)

compound	steric energy	heat of formation
oxirane (1)	9.5575	−12.58
2-methyloxirane (2)	9.8742	−22.63
cis-2,3-dimethyloxirane (3)	12.7013	−30.17
trans-2,3-dimethyloxirane (4)	10.2775	−32.60
epoxyisolongefolene (5)	46.1337	−58.70
1-(*p*-bromophenyl)-1,2-epoxycyclohexane (6)	13.6462	*a*
trans-4-*tert*-butyl-1-phenyl-1,2-epoxycyclohexane (7)	17.3730	*a*
chamigrene epoxide (8)	37.7023	−40.32
cyclohexene oxide (9)	16.3342	−32.96
cyclooctene oxide (10)	24.3703	−37.75
norbornene oxide (11)	36.7196	−12.58

[a] Heat of formation parameters for aromatics are not included in MM2.

similarity of the epoxide moieties in these three structures suggests that any systematic error would result in a consistent difference between calculation and experiment, but such consistency is not observed. We therefore concluded that the agreement between experiment and calculation for the data in Table VII did not dictate further modification of the epoxide parameters. The standard deviation is 1.50 kcal/mol, about three times larger than the errors reported by Allinger for alcohols and ethers.[22] This reflects the small number of available experimental values and suggests that some of the experimental data may be in error. The possibility that our energy minimizations had not afforded the lowest energy conformations was ruled out by running the calculations with the RIPS routine.[4] The interdependence between structural parameters and heat of formation parameters is relatively small in MM2 calculations, so it should become possible to refine the latter when additional experimental data become available. A summary of calculated heats of formation and steric energies for all structures is presented in Table VIII.

The good agreement obtained between experimental and calculated structures for a series of epoxides demonstrates that we have successfully extended the MM2 force field to include this functional class of compounds. Structural results obtained with MM2 calculations of other epoxides with these parameters should be highly reliable. Our calculated heats of formation may exhibit moderate (and possibly systematic) errors on the order of 1 kcal/mol, but relative energies for any set of related structures should again be reliable.

Acknowledgment. We thank Professor N. L. Allinger, University of Georgia, for helpful suggestions and discussions during the course of this work. We also thank Dr. David M. Ferguson, USF, for invigorating discussions and assistance with the RIPS procedure and Dr. B. D. Silverman, IBM, T. J. Watson Research Center, who provided us with a partial set of parameters that he had developed for bay-region epoxides. This work was assisted by University Computing Services at the University of South Florida, which provided technical support and extensive computing time.

Supplementary Material Available: For each compound reported, the MM2-optimized coordiantes and summary of components of the total energy (18 pages). Ordering information is given on any current masthead page.

---

(21) Timofeeva, L. P.; Luk'yanova, V. A.; Kozina, M. P.; Stepanova, N. V. *Kalorim. Khim. Thermdin., Dokl. Vses. Konf., 10th* **1984**, *1*(2), 193.

(22) Allinger, N. L.; Chung, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 6798.

Cycloadditions of Cycloocta[*def*]biphenylene-1,4-dione and Other Quinones: Evidence for the Importance of Charge-Transfer Contributions to the Transition State

Charles F. Wilcox, Jr.,* Kevin R. Lassila,[1] and Corraine E. Young

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

Received January 10, 1989

Cycloadditions of the title compound (5) proceed more slowly than expected for a dienophile with two activating substituents. The Hückel-based transition-state model developed by Carpenter and Wilcox indicated that the aromaticity of 5 played no significant role in its reactivity. This model also indicated that the geometrical distortions present in 5 would tend to *increase* rather than decrease its rate of cycloaddition. A correlation between the rate of reaction of 5 and several model quinones with their reduction potentials suggest that there is a significant degree of charge transfer (ca. 0.4*e*) in the transition state. Explicit consideration of charge-transfer contributions to the transition state provided an excellent fit to the experimentally observed rates.

Introduction

Polycyclic π-hydrocarbons containing multiply fused $4N$- and $(4N + 2)$-membered rings[2-5] frequently behave in ways that defy conventional chemical intuition. For example, cycloocta[*def*]biphenylene[4a,b] (1) displays thermal stability typical of an aromatic species, reactivity of a polyolefin, and a diminished diatropism consistent with increased

---

(1) Based on the Ph.D. Dissertation submitted by K.R.L. to the Cornell Graduate School, 1988.

(2) (a) Wilcox, C. F., Jr.; Weber, K. A. *J. Org. Chem.* **1986**, *51*, 1088–1094. (b) Wilcox, C. F., Jr.; Weber, K. A. *Tetrahedron* **1985**, *41*, 4425–4436. (c) Wilcox, C. F., Jr.; Weber, K. A.; Abruna, H. D.; Cabrera, C. R. *J. Electroanal. Chem.* **1986**, *198*, 99–105.

(3) (a) Wilcox, C. F., Jr.; Blain, D. A.; Clardy, J.; Xu, C.-F. *J. Org. Chem.* **1987**, *52*, 2635–2639. (b) Wilcox, C. F., Jr.; Blain, D. A.; Clardy, J.; Van Duyne, G.; Gleiter, R.; Eckert-Maksic, M. *J. Am. Chem. Soc.* **1986**, *108*, 7693–7702. (c) Wilcox, C. F., Jr.; Blain, D. A. *Tetrahedron* **1986**, *42*, 6389–6398.

(4) (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohman, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2532–2533. (b) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; grohmann, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914–1920. (c) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889–2895. (d) Obendorf, S. K.; Wilcox, C. F., Jr.; Grantham, G. D.; Hughes, R. E. *Tetrahedron* **1976**, *32*, 1327–1330. (e) Bekarian, P. G. Ph.D. Dissertation, Cornell University, 1981.

(5) (a) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351–356. (b) Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1983**, *105*, 7191–7192. (c) Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195–7200.

0022-3263/89/1954-5035$01.50/0