nitrobenzenesulfinate, 49558-57-8; o-nitrophenylthioacethydrazide, 4871-40-3.

References and Notes

(1) For an extensive review see P. N. Preston and G. Tennant, *Chem. Rev.*, **72**, 627 (1972).
(2) F. Arndt, B. Eistert, and W. Partale, *Chem. Ber.*, **60**, 1364 (1927).
(3) E. Giovannini and P. Portmann, *Helv. Chim. Acta*, **31**, 1381 (1948).
(4) J. A. Moore and D. H. Ahlstrom, *J. Org. Chem.*, **26**, 5254 (1961).
(5) E. C. Taylor and D. R. Eckroth, *Tetrahedron*, **20**, 2059 (1964).
(6) J. F. J. Engbersen and J. B. F. N. Engberts, *Syn. Commun.*, **1**, 121 (1971).
(7) Ortho nitro groups can act as good internal nucleophiles; see S. Kim, S. S. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **92**, 5452 (1970), and references cited therein.
(8) A. M. van Leusen and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **84**, 151 (1965).
(9) J. B. F. N. Engberts and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **84**, 942 (1965).
(10) When o-nitrobenzenesulfinic acid is heated in ethanol under reflux for several hours, nitrobenzene is formed together with sulfur dioxide: A. Wagenaar, unpublished results.
(11) For a review of the Smiles rearrangement, see J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951).
(12) For the p-nitro substituted isomer, this absorption is found at δ 5.33 ppm in $CDCl_3$. The exact origin of the low-field shift of the methine proton absorption in **3** is under investigation.
(13) A. M. van Leusen and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**, 67 (1970).
(14) The uv absorption between 300 and 400 nm of a dilute solution of **3** in 60% (v/v) dioxane–water changed less than 2% after 3.5 hr at room temperature.
(15) Complete hydrogen–deuterium exchange of the methine proton of **3** was observed within 10 min in 60% (v/v) dioxane–deuterium oxide at 36°. Under these conditions exchange is much slower for the p-nitro isomer (35% exchange after 17 hr). It is not clear, however, whether in this neutral medium exchange is primarily acid catalyzed.
(16) J. B. F. N. Engberts and B. Zwanenburg, *Tetrahedron*, **24**, 1737 (1968).
(17) A series of arylsulfonylmethyl triflates has been prepared previously: K. Hovius and J. B. F. N. Engberts, *Tetrahedron Lett.*, 2477 (1972). The triflate **13** is very sensitive toward nucleophilic substitution by nonbasic nucleophiles as demonstrated by the almost instantaneous reaction with LiCl to give **12** in acetone–DMF (4:1).
(18) Owing to their instability, simple α-oxo sulfones, $R_1COSO_2R_2$ have not been isolated thus far. Only when the carbonyl group is made less prone to nucleophilic attack by appropriate substitution may α-oxo sulfones to be obtained: (a) R. J. Gaul and W. J. Fremuth, *J. Org. Chem.*, **26**, 5103 (1961); (b) A. Senning, O. N. Sorensen, and C. Jacobson, *Angew. Chem.*, **80**, 704 (1968); (c) T. Olijnsma, J. B. F. N. Engberts, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 897 (1970).
(19) T. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **89**, 696 (1970).
(20) The decomposition of **2** in 40% (v/v) dioxane–water containing 0.8825 *N* HCl was followed at 470 nm and found to be much slower than that of **1** in this medium.
(21) P. Karrer and J. Schuker, *Helv. Chim. Acta*, **28**, 820 (1945).
(22) F. L. Rose and B. R. Wilson, British Patent 782,420 (1957); *Chem. Abstr.*, **52**, 2907*i* (1958).

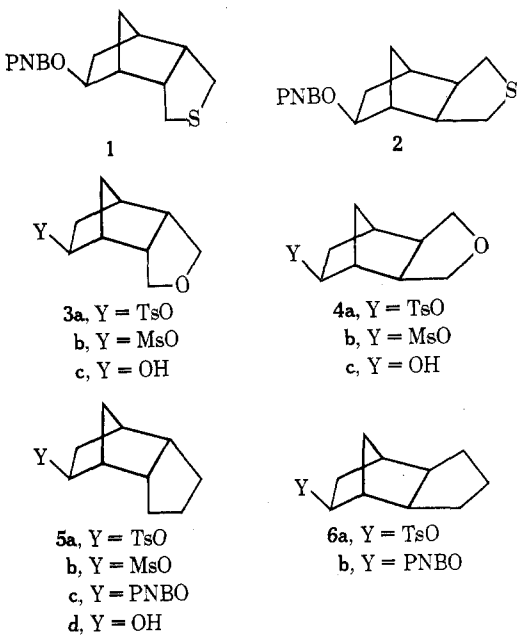
Remote Oxygen Participation in the Solvolysis of *endo*-4-Oxatricyclo[5.2.1.$0^{2,6}$]dec-8-yl Methanesulfonate

Pelham Wilder, Jr.,* and Carol Van Atta Drinnan[1]

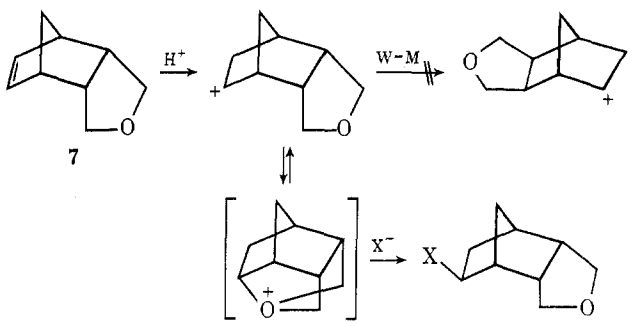
Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received August 17, 1973

The report of significant participation by remote sulfur in the *endo*-4-thiatricyclo[5.2.1.$0^{2,6}$]decane system (**1**)[2] prompted the reexamination of analogous oxygenated compound **3** and its skeletal isomer **4** to determine if similar oxygen participation could be detected. In a preliminary investigation of this problem Cash found no kinetic evidence for participation in the ethanolysis of **3a–6a**, but he was severely hampered by the low purity of his starting esters.[3] It had previously been noted that addition of acidic reagents to **7** proceeded with little rearrangement to the exo-fused ring and it was proposed that intervention of an ion such as **8** prevented the expected rearrangement (see Scheme I).[4] The same ion **8** should be formed in solvolysis of **3**, either concurrent with departure of the leaving group or subsequent to formation of the secondary carbonium ion.



Scheme I



The phenomenon of neighboring group assistance by oxygen is well documented;[5] participation by the oxygen atom of sulfinyl,[6] carbonyl,[7] hydroxyl,[8] and ether[9] groups has been described. Ether participation has been extensively studied in the carbohydrate field,[10] but until recently investigations of such oxygen participation in conformationally rigid molecules other than carbohydrates have been lacking. Martin and Bartlett found no participation of bridge oxygen in solvolysis of **9** where the sole

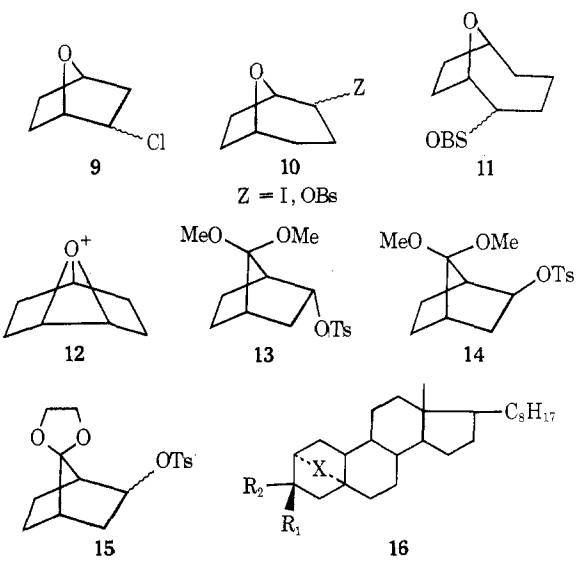


Table I

Compd	Temp, °C	$k \times 10^5$, sec^{-1} [a]	Rel k	ΔH,* kcal/mol	ΔS,* eu
3b	52.96	10.9 ± 0.5	2.53	19.2 ± 0.3[b]	−18.0 ± 0.9[b]
	65.65	36.2 ± 0.6			
	75.90	81.3 ± 0.1			
4b	75.90	1.77 ± 0.09	0.05	30.8 ± 1.6	+7.7 ± 4.6
	85.70	6.16 ± 0.21			
5b	52.96	2.63 ± 0.17	1.00	23.3 ± 0.6	−8.2 ± 1.8
	65.65	13.2 ± 0.1			
	75.90	32.2 ± 2.1			
	85.75	79.5 ± 2.8			
5a	59.7	16.9	3.84	26.0	−2.2
	39.8	1.30			
	(74.8)	(97.3)[c]			
6a	74.8	25.3	1.00	25.8	−1.1
	59.7	4.59			
	50.1	1.35			

[a] Each rate constant is the average of two or more runs; the indicated precision is the variation of the rate constant for each run from the average. [b] The indicated precision is the standard deviation. [c] Extrapolated from data at other temperatures.

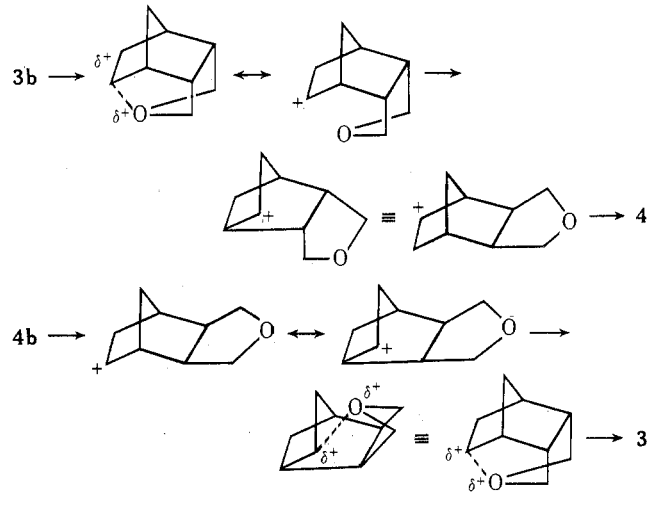
product arose from rearrangement of the carbon skeleton.[11] In oxygen-bridged compounds with larger rings (**10** and **11**) Paquette and coworkers have observed reaction products due to rearrangement *via* intermediate oxonium ions such as **12**.[12] Gassman and coworkers have shown MeO-4 participation to be important in the solvolysis of **13**, while it was negligible in the case of **14** and both isomers of **15**.[13] In the steroidal system **16** Tanida and coworkers found only a rate-retarding effect when oxygen was the heteroatom, while the endo-substituted sulfide (R_1 = Br or OMs) reacted 10^{10} times faster than the corresponding ether.[14] It was also noted that the exo–endo ratio in the ethers was very close to that of the parent norbornyl system, further indicating the lack of oxygen participation.

From these data it is apparent that rate enhancement due to remote oxygen participation in solvolysis of **3b** should not be expected to be as large as was found for **1**. Oxygen is less effective than sulfur as a neighboring group owing to its greater inductive rate-retarding effect, lower ability to donate electron pairs, and smaller size that decreases efficient overlap at a remote carbonium ion center. The results of solvolysis of **3b**, **4b**, and **5b** in 75% by weight aqueous dioxane are reported in Table I, along with results for methanolysis of **5a** and **6a** obtained by Takeuchi and coworkers.[15]

The 2.5-fold rate acceleration produced by changing from an *endo*-trimethylene bridge to an oxygenated bridge is not of itself sufficient to indicate oxygen participation, even though Schleyer and Lancelot have proposed that "the detection of any rate enhancement due to anchimeric assistance, *no matter how small*, is indicative of strong participation by the neighboring group."[16] The steric acceleration of solvolysis attributable to the endo-fused oxygenated ring should be approximately the same as that found for the trimethylene-bridged compound. The rate difference of 50 between **3b** and **4b**, while much smaller than the 1000-fold difference between **1** and **2**,[2] is 13 times as great as the rate difference of 3.84 between **5a** and **6a** and 35 times as great as the 1.4-fold difference in rates of solvolysis of **5c** and **6b**.[2] The rate enhancement due to the endo-fused hetero bridge derived in this way is definitely suggestive of remote oxygen participation.

The products arising from solvolysis of **3b** were 90–93% alcohol **3c** and 7–10% alcohol **4c**; from **4b** were obtained 40% alcohol **3c** and 60% alcohol **4c**. In each case recovery of unreacted ester revealed no direct interconversion between **3b** and **4b** prior to solvolysis. Although no definitive evidence is yet available on the question, it is assumed that the exo skeleton **4** is more stable than the endo skeleton **3** as is the case of the carbocyclic compounds.[17] At least part of the ion derived from **3b** leaks to the open carbonium ion and rearranges to the exo ion as shown in Scheme II. The products from **4b** indicate, however, that much of the initially formed carbonium ion survives long enough to undergo rearrangement to the stabilized oxonium ion which leads to products of endo configuration. Thus these experiments have demonstrated remote oxygen participation that is of a modest magnitude kinetically, but is extremely important in product determination after the initial ionization step.

Scheme II



Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Infrared spectra were obtained on Perkin-Elmer 137 or 237 double-beam spectrophotometers. Nmr spectra were recorded on a Varian T-60 spectrometer. Analytical glpc analyses were performed on a Varian Aerograph Series 1200 instrument.

8-*exo*-Hydroxy-*endo*-4-oxatricyclo[5.2.1.$0^{2,6}$]decane (3c). Following the hydroxymercuration–demercuration procedure of Brown,[18] 29.1 g (0.214 mol) of **7**[4] was added with stirring to a solution of 68.3 g (0.214 mol) of mercuric acetate in 428 ml of 50% aqueous THF. The solution changed rapidly from orange to pale yellow and was stirred for 1.5 hr before work-up with 107 ml of 6 *N* NaOH and 107 ml of 1 *M* $NaBH_4$ in 6 *N* NaOH. The mixture was stirred overnight. After separation of layers, the aqueous portion was saturated with NaCl and extracted twice with ether; the combined organic layers were dried over $MgSO_4$. Removal of solvents under reduced pressure yielded 31.0 g (94%) of **3c**. The crude product was sublimed to give a hygroscopic, waxy solid, mp 103° [lit.[19] bp 102–103° (0.4 mm)]. The endo position of the ether ring was confirmed by Chugaev degradation of **3c** to **7**, a reaction

sequence that proceeds without rearrangement in the dicyclopentadiene system.[17]

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 69.90; H, 9.22.

Methanesulfonate 3b. The mesylate was prepared by reaction of a slight excess of methanesulfonyl chloride with **3c** in pyridine in the cold. The ester, recrystallized from methanol, had mp 105.5–106.0°.

Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.75; H, 6.90; S, 13.78. Found: C, 51.72; H, 6.95; S, 13.71.

8-*exo*-Hydroxy-*exo*-4-oxatricyclo[5.2.1.$0^{2,6}$]decane (4c). Following the procedure used for the preparation of **3c**, 10.0 g of pure *exo*-4-oxatricyclo[5.2.1.$0^{2,6}$]-8-decene[4] yielded 5.28 g (47%) of **4c**, bp 87.5° (0.25 mm)–90° (0.30 mm) [lit.[4] bp 95–97° (0.7 mm).

Methanesulfonate 4b. The mesylate, prepared from **4c** in the manner described for **3b**, formed shiny white platelets, mp 56.4–56.7°, after recrystallization from petroleum ether (bp 30–60°).

Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.75; H, 6.90; S, 13.78. Found: C, 51.87; H, 6.99; S, 13.75.

Methanesulfonate 5b. The ester, prepared from the alcohol 8-*exo*-hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**5d**)[19] and methanesulfonyl chloride in pyridine, was an oil which decomposed upon distillation.

In a second preparation, the reaction mixture from 5.0 g of alcohol **5d** and 5.0 g of methanesulfonyl chloride in 40 ml of anhydrous pyridine was stored in a freezer overnight and then was poured over ice to which had been added 46 ml of concentrated HCl. The orange oil which separated was taken up in ether and the aqueous portion was extracted three times with ether. The combined ethereal portions were washed twice with water, dried over $MgSO_4$, and then filtered. After removal of solvent, a final removal was conducted under high vacuum at room temperature. The yield was 6.8 g (90%) of ester as a slightly discolored liquid.

Anal. Calcd for $C_{11}H_{18}SO_3$: C, 57.45; H, 7.83. Found: C, 57.75; H, 7.90.

Kinetic Measurements. Reagent grade *p*-dioxane was rigorously purified by the method of Wiberg.[20] Typically 45.0 g of dioxane was diluted with 15.0 g of deionized water to prepare the 75% aqueous dioxane. Esters were weighed into 50-ml volumetric flasks so that solutions approximately 1×10^{-2} *M* in ester would be obtained when solvent was added. The samples were divided into ten screw-cap test tubes and incubated in a constant-temperature bath together with a 5-ml solvent blank. Samples were withdrawn at intervals, frozen in Dry Ice–acetone, washed out with water, and titrated immediately with 1×10^{-2} *M* NaOH to a phenolphthalein end point. Infinity values for **5b** and **3b** were constant at 100 and 90% of theoretical, respectively; the theoretical infinity value for **4b** was used after it was discovered that solvent, alone or pyridine buffered, developed considerable acidity over the reaction time required for 10 half lives. Plots of log $(A_\infty - A_t)$ *vs.* time were linear; the slopes were determined by calculation of the least-squares line fitting the experimental points.

Product analysis was accomplished by gas chromatography on a 5 ft × 0.125 in. 20% FFAP column at 180° with a flow rate of 25 ml/min. Samples taken at various times from kinetic runs at different temperatures showed essentially constant ratios of **3c** and **4c**, depending on the starting ester; no traces of the endo epimers of **3c** and **4c** (independently synthesized) were detected. In an experiment to recover unreacted **3c**, 150 mg of ester in 50 ml of solvent was incubated at 75.90° for 7–8 min, poured into ice water, and extracted continuously with ether. After drying and evaporation, crystals, mp 100–102.5°, were recovered: ir spectrum identical with that of authentic **3c**; mmp with **3c**, 88–93°; mmp with **4c**, 40–93°. Similarly 150 mg of **4c** in 50 ml of solvent was incubated at 75.90° for 4.5 hr, poured into ice water, and extracted. Crystals melting at 55.2–56.2° were recovered: ir spectrum identical with that of authentic **4c**; mmp with **4c**, 55.0–56.0°; mmp with **3c**, 40–68°.

Registry No. 3b, 43187-55-9; **3c**, 43187-56-0; **4b**, 43187-57-1; **4c**, 43187-58-2; **5b**, 43187-59-3; **5d**, 10271-45-1; **7**, 43187-61-7; *exo*-4-oxatricyclo[5.2.1.$0^{2,6}$]-8-decene, 43187-62-8.

References and Notes

(1) National Science Foundation Predoctoral Fellow, 1970–1972.
(2) R. F. Gratz and P. Wilder, Jr., *Chem. Commun.*, 1449 (1970).
(3) D. J. Cash, Ph.D. Dissertation, Duke University, 1964.
(4) C. F. Culberson, J. H. Seward, and P. Wilder, Jr., *J. Amer. Chem. Soc.*, **82**, 2541 (1960).
(5) For reviews of neighboring-group assistance see W. Lwowski, *Angew. Chem.*, **70**, 483 (1958); B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).
(6) (a) M. Cinquini, S. Colonna, and F. Montanari, *Tetrahedron Lett.*, 3181 (1966); (b) H. Hogeveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc. C*, 1585 (1966).
(7) (a) C. N. Lieske, E. G. Miller, Jr., J. J. Zeger, and G. M. Steinberg, *J. Amer. Chem. Soc.*, **88**, 188 (1966); (b) J. S. Brimacombe, F. Hunedy, and L. C. N. Tucker, *J. Chem. Soc. C*, 1381 (1968); (c) M. S. Newman and A. L. Leegwater, *J. Amer. Chem. Soc.*, **90**, 4410 (1968); (d) H. D. Burrows and R. M. Topping, *Chem. Commun.*, 904 (1969).
(8) (a) D. L. H. Williams, *Tetrahedron Lett.*, 2001 (1967); (b) L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **90**, 5159 (1968); (c) B. Capon, S. T. McDowell, and W. V. Raftery, *Chem. Commun.*, 389 (1971); (d) M. Miljkovic, D. Miljkovic, A. Jokic, V. Andrejevic, and E. A. Davidson, *J. Org. Chem.*, **37**, 2536 (1972).
(9) (a) E. Allred and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 3991, 3998, 4008, 4012 (1967); (b) J. R. Hazen and D. S. Tarbell, *Tetrahedron Lett.*, 5927 (1968); (c) J. R. Hazen, *ibid.*, 1897 (1969).
(10) (a) N. A. Hughes and P. R. H. Speakman, *J. Chem. Soc. C*, 1182 (1967); (b) C. F. Gibbs and H. J. Jennings, *Can. J. Chem.*, **48**, 2734 (1970); (c) J. S. Brimacombe and O. A. Ching, *J. Chem. Soc. C*, 1642 (1968); (d) *ibid.*, 964 (1969); (e) *Carbohyd. Res.*, **9**, 287 (1969).
(11) J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957).
(12) (a) L. A. Paquette and P. C. Storm, *J. Org. Chem.*, **35**, 3390 (1970); (b) L. A. Paquette and M. K. Scott, *J. Amer. Chem. Soc.*, **94**, 6760 (1972); (c) L. A. Paquette, I. R. Dunkin, J. P. Freeman, and P. C. Storm, *ibid.*, **94**, 8124 (1972).
(13) (a) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968); (b) P. G. Gassman and J. G. MacMillan, *J. Amer. Chem. Soc.*, **91**, 5527 (1969).
(14) T. Tsuji, T. Komeno, H. Itani, and H. Tanida, *J. Org. Chem.*, **36**, 1648 (1971).
(15) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Jap.*, **38**, 1318 (1965).
(16) P. v. R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 4297 (1969).
(17) G. W. Wright, Ph.D. Dissertation, Duke University, 1971.
(18) H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem.*, **35**, 1844 (1970).
(19) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Amer. Chem. Soc.*, **82**, 2351 (1960).
(20) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960.

Rate–Strain Relationships in the Oxidation of Small-Ring Cyclic Olefins with Peracid

Louis E. Friedrich* and Rocco A. Fiato[1]

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received October 9, 1973

The kinetics of epoxidation of only two strained olefins have been reported in the literature.[2a-c] In peracetic–acetic acid solution at 25.8°, cyclobutene epoxidizes 6.3 times slower than cyclohexene and 9.6 times slower than cyclopentene.[3] Norbornene, on the other hand, epoxidizes 1.2 times faster than cyclohexene at 25° with perlauric acid in chloroform.[4] Since norbornene epoxidizes 99.5% exo,[5] the corrected rate constant for norbornene per olefin side is 2.4 times faster than cyclohexene. Even though cyclobutene and norbornene are 30.6 and 27.2 kcal/mol strained,[6] their rate constants for epoxidation are within a factor of 10 (1.25 kcal/mol) of the rate constants for the much lesser strained cyclopentene through cycloheptene systems.[2a] There appears to be no rate–strain relationship for epoxidation reactions.

In light of the above results, we expected that the oxidation of cyclopropenes with peracid might be atypical and would be a severe test of the previously observed results that the rate of epoxidation is independent of olefin strain. Specifically, the 55 kcal/mol strain[6] in cyclopropenes is twice the strain of the olefins whose epoxidation kinetics have previously been studied. Furthermore, this abnormally large strain has caused the double bond in these compounds to have a characteristic high reactivity toward various reagents.[7] If the loss of even a fraction of this 55 kcal/mol of strain energy were not compensated by