at 90 MHz were satisfactory. In all cases p-dimethoxybenzene was the internal standard. The quartets at δ 1.942 and 2.317 due to the H_4 protons were used for **7a** and **8a** respectively. Doublets at δ 1.150 and at δ 1.087 due to the 5-CH_3 group were used for **7b** and **8b** respectively. Quartets at δ 2.330 and at δ 1.966 (H_4 protons) and singlets at δ 2.188 and 2.100 (CH_3CO–) were used for **10**, **9**, **11**, and **8c**, respectively. The multiplet at δ 5.49–5.10 (H_1 and H_3) and the triplet at δ 2.56 (H_4 protons) were used for **7d** and **8d**, respectively.

Rate of Reaction of CAN with Carbonyl Compounds. The rate of disappearance of CAN in solutions containing the various carbonyl compounds were determined by iodometric analysis in the absence and in the presence of 1,3-butadiene. With acetone, the half-life time of CAN was 5 h in the presence and 17 h in the absence of 1,3-butadiene. Corresponding values for 2-butanone were 0.75 and 2.3 h. With ethyl acetoacetate the disappearance of CAN was almost instantaneous in the presence of 1,3-butadiene, whereas in the absence of diene only 58% of CAN was reduced after 30 min. With 3-methyl-2-butanone reduction of CAN was complete after 8 and 24 h, in the presence and in the absence of 1,3-butadiene, respectively.

Acknowledgment. Thanks are due to the Italian National Council of Research (CNR) and the Ministero della Pubblica Istruzione for financial support.

Registry No. **7a**, 100431-93-4; **7b** (isomer 1), 100431-95-6; **7b** (isomer 2), 100431-96-7; **7d**, 100432-01-7; **8a**, 100431-94-5; **8b**, 100431-92-3; **8c**, 100431-97-8; **8d**, 100432-02-8; **9**, 100431-98-9; **10**, 100431-99-0; **11**, 100432-00-6; **12**, 33626-83-4; CAN, 16774-21-3; acetone, 67-64-1; 2-butanone, 78-93-3; 3-methyl-2-butanone, 563-80-4; ethyl acetoacetate, 141-97-9; 1,3-butadiene, 106-99-0.

Convergent Functional Groups. 2. Structure and Selectivity in Olefin Epoxidation with Peracids

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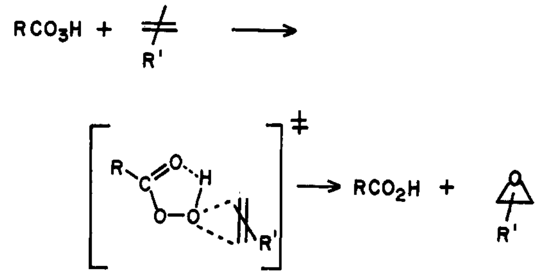
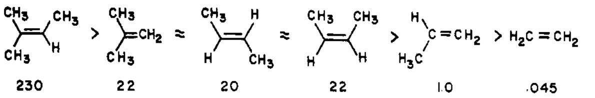
Problems associated with selectivity in olefin epoxidation with peracids are discussed, with special regard to cis/trans selectivity. The development of a new class of peracids is described in which steric effects become magnified and compete with electronic ones. These reagents show high selectivity for cis olefins in the presence of trans or 1,1-disubstituted derivatives. The possible origins of selectivity are outlined, and these are related to proposals concerning the transition structure for oxygen transfer with peracids.

Introduction

Stereoelectronic effects[1] have come to dominate mechanistic thinking in this decade in much the same way as the Woodward–Hoffmann rules did the last one, with good reason. These effects provide a Rosetta stone for translating structure into reactivity. This article is concerned with these notions as they apply to the Prilaschajew reaction, i.e., the peracid epoxidation of olefins (eq 1).



This reaction has been the subject of numerous mechanistic enquiries,[2] the results of which are summarized in the equation above: intramolecular hydrogen bonding in the peracid fixes the orientation of the O–O bond; the olefin approaches the system along the line of the O–O bond as though an S_N2 reaction were being performed on the terminal oxygen;[3a] oxygen transfer occurs without detectable intermediates. One of the important synthetic consequences of such a reaction trajectory is that the reaction rate appears immune to steric effects. Little opportunity exists for interactions between groups on the olefin and the R of the peracids. Accordingly, most cis-disubstituted olefins react only slightly (1.1–2.2 times) faster than their trans counterparts,[3b] regardless of peracid structure, and 1,1-disubstituted olefins react at rates comparable to either the cis or trans isomers (eq 2; relative rates of olefin epoxidation with peracids[3c] are given below the structures).



This consistency has permitted the reaction to survive as a practical synthetic method for some 75 years. The inefficiency of asymmetric peracids in providing optically active epoxides is also understandable from the transition structure of eq 1. An asymmetric environment provided by substituents at the α-carbon of a peracid is ill-placed to influence the approach and alignment of an olefin near the distal oxygen. In this respect, then, cis/trans selectivity

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(1) Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon Press: Oxford, 1983.

(2) For reviews with leading references see: Rebek, J., Jr. *Heterocycles* **1981**, *15*, 517–545; Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734–750.

(3) (a) See, for example: Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63–73 and literature cited therein. (b) Stumpf, W.; Rombusch, K. *Justus liebigs Ann. Chem.* **1965**, *687*, 136–199. (c) Swern, D. *Org. React.* **1953**, *7*, 378–433.

(4) (a) A preliminary account of this work has appeared: Rebek, J., Jr.; Marshall, L.; Wolak, R.; McManis, J. *J. Am. Chem. Soc.* **1984**, *106*, 1170–71; (b) Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985** *107*, 7426–7481.

0022-3263/86/1951-1649$01.50/0

Table I. Rate Ratios for Epoxidation ($CDCl_3$; 25 °C)

	k_{cis}/k_{trans}			
peracid of	2-octenes	t-BuC(H)=C(H)Et	cyclododecenes	$PhC(CH_3)=CH_2$/ t-$PhCH=CHCH_3$
MCPBA	1.2	1.0	0.47[a]	1.0
3a	1.9	1.6	0.54	0.7
3b	1.3	1.0	0.36	0.7
3c	2.2	1.8	0.72	1.6

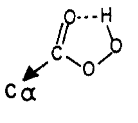
[a] Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295–296.

is related to enantioselectivity and one of our ultimate goals has been to develop peracid reagents capable of asymmetric epoxidation.

Given the remarkable success of the Sharpless[5] reagent in producing asymmetric epoxides, some justification may be required. Although a reagent more synthetically useful is hard to imagine, the structure of the active species in the Sharpless system remains unknown even 5 years after its discovery. Subtle changes in stoichiometry[6] or hydration[7] lead to seemingly unpredictable changes in selectivity for allylic alcohols and sulfides; generalizations are difficult to formulate. The peracids, on the other hand, provide a well-defined structural problem, the solution of which ought to provide reliable approaches to the more general questions concerning stereoelectronic effects at carboxyl oxygen.[8]

Peracids with U Shapes

If the problem of peracid selectivity be posed as one of imbedding the distal oxygen into a controlled microenvironment, then some serious structural work would be anticipated. The first bond away from the carboxyl carbon points in precisely the wrong direction (A) and at least a U turn must be engineered into the structure (B) to bring influential groups to the site of oxygen transfer. A freely rotating system cannot be useful, since only a few (unlikely) conformations would bring the two ends of the molecule together.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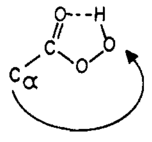
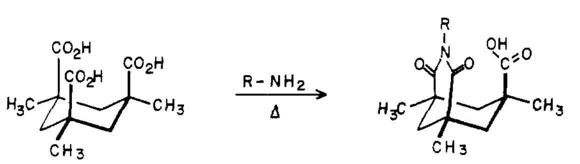

B

A promising candidate for a rigidly maintained shape was provided by the unusual triacid 1 first prepared by Kemp[9] (eq 3). The three equatorial methyl groups force the carboxyls into a triaxial conformation and maintain a U-shaped relationship between any two acid functions.


1 2 (3)

Condensation of the triacid or its derivatives with amines leads to imides 2 in which the R groups are positioned not far from the carboxyl destined to become the peracid. A number of these imides were prepared from bulky and asymmetric aliphatic amines. Yet their peracid derivatives all failed simple tests of selectivity in olefin epoxidation. With aromatic amines having ortho substitutents (3) some encouraging results were obtained. The ortho substitutents maintain a position away from the carboxyl group and thereby effectively stop rotation about the C_{aryl}–N bond.[4b] In such structures groups meta to the nitrogen become suspended above the carboxylic acid hydrogen. A number of such acids were converted to the respective acid chlorides, and their peracids were generated in situ with H_2O_2/pyridine.[10] Using direct competition between the indicated olefin pairs as the probe for selectivity, the figures of Table I were obtained.

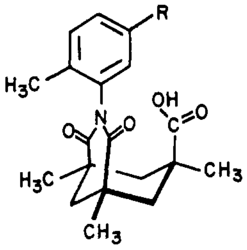

3a R = CO_2Me
3b R = C_6H_5
3c R = CON (*i* Pr)$_2$

Table II. Relative Epoxidation Rates

peracid of	1,2/1,α[a]	t-BuC(H)=C(H)Et (k_{cis}/k_{trans})
4	0.88	0.7
MCPBA	0.91	1.0

[a] 1,2 = 1,2-epoxycyclohexane; 1,α = 1,2-epoxymethylcyclohexane (1-oxaspiro[2,5]octane).

As the meta substituent was increased in size, few changes were detected in the selectivity. Only the diisopropyl amide showed promise, but its selectivity–compared to *m*-chloroperbenzoic acid (MCPBA)—was modest. It appeared likely that small angle distortions near the base of these molecules led to divergence between the peracid function and the remote group. This suggested another approach to defining the steric environment of the distal oxygen of the peracid. Specifically, in structures such as 4 the aromatic portion presents a flat wall in the region beside and beyond the carboxyl function that is to become the peracid. Condensation of the acid chloride anhydride[9] 5 with the diamine 6 did indeed produce the acylated perimidine 4 in excellent yield (eq 4). It was converted to the corresponding acid chloride which was used to generate the peracid in situ. However, as shown in Table II, initial epoxidation results with this were discouraging. Similar results were obtained with the structure from *o*-phenylenediamine.

An altogether different means of probing steric effects in peracid epoxidations is possible with the use of unusual olefins. For example, betweenanenes such as 7 are described by Marshall[11] as inert to peracids, but the sesquinorbornene 8 is described by Bartlett[12] as unexceptional in this reaction. We examined some olefins between these

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[5] Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974–5976.

[6] Lu, L. D.-L.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728–731.

[7] Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 8188–8193.

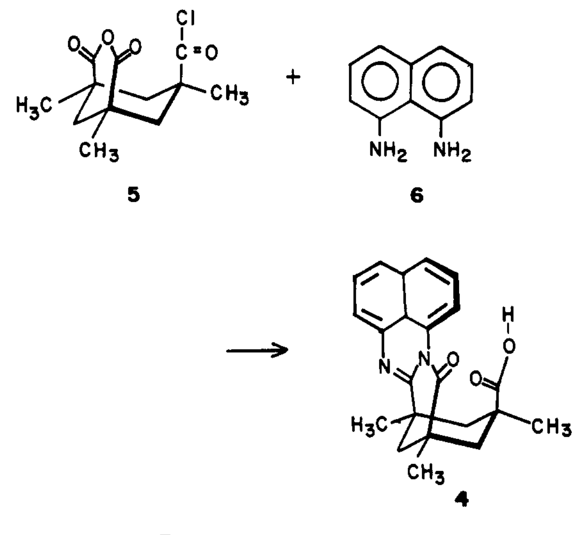
[8] Gandour, R. *Bioorg. Chem.* **1981**, *10*, 169–176.

[9] Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140–5143.

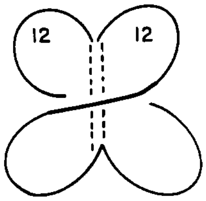
[10] Nedelec, J. Y.; Sorba, J.; Lefort, D. *Synthesis* **1976**, 821–823.

[11] Marshall, J. A.; Black, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 7581–7583.

[12] Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383–1390. For an unusual steric effect see: Schneider, H.-J.; Becker, N.; Philippi, K. *Chem. Ber.* **1981**, *114*, 1562–1566.


5 **6** **4**

(4)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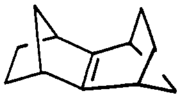
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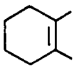
structural extremes: the dimethylcyclohexene (**9**), isopropylidenecyclohexane (**10**), the octahydronaphthalene (**11**), and cyclohexylidenecyclohexane (**12**). These four alkenes present a range of steric effects to electrophiles from open "sides" to open "ends". Competitions were performed with the peracids derived from **3** and the results are shown in Table III.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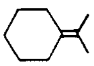
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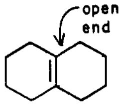

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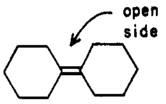
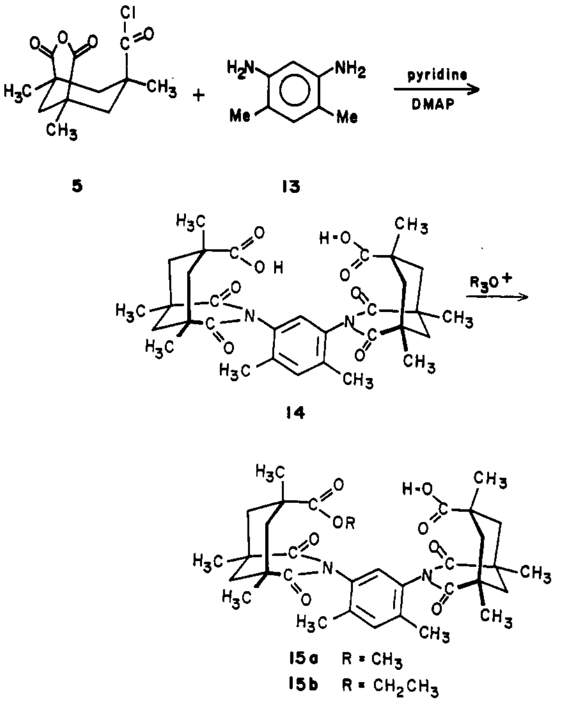


12

Again, results were meager but sustaining and two trends emerged. Firstly, open-sided olefins tend to be preferred to open-ended ones, and secondly, when both olefins have the same open-ended- or sidedness, a modest preference is seen for the least hindered olefin. It should be emphasized that these studies are experimentally quite demanding owing to the sinister autoxidation of these highly reactive alkenes. Although care was taken to prevent such side reactions, the low selectivities observed require cautious interpretation.

Peracids with C Shapes

At the very least these results suggested that a radical new departure was required. Specifically, a design was required in which groups were not suspended near, but actually *in front of the distal oxygen of the peracid*. This notion materialized in the form of the product of a double condensation between the xylidenediamine (**13**) and the triacid **5** (eq 5).

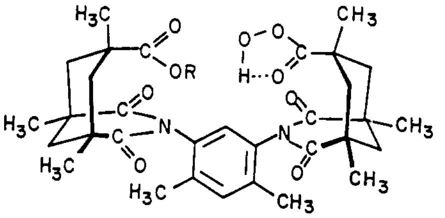


5 **13** **14**

15a $R = CH_3$
15b $R = CH_2CH_3$

(5)

Structure **14** is a diacid with 8 seemingly passive methyl groups. Each has its purpose: by preventing epimerizations or rotations, these methyls enforce the convergence of the two carboxyl functions. The unique C shape of this molecule permitted the preparation of the monoesters **15** by reaction with the appropriate oxonium ions,[13] and peracids derived from these materials did indeed show the desired cis selectivity in competition experiments. In addition, they showed a preference for cis olefins vs. 1,1-disubstituted olefins (Table IV).



Even within cis-disubstituted olefin pairs a steric effect for the reaction could be detected. For example, in competition studies between 2-octenes and dimethylhexenes (Table V), a preference is shown for the less hindered octene; little such preference can be detected with MCPBA.

As the existence of steric effects was gradually revealed, it seemed likely that cases could be found in which steric effects would ultimately overwhelm the electronic ones that dominate the reaction selectivity of conventional peracids. Generally, electron-withdrawing groups in the olefin reduce epoxidation rates and electron-releasing groups increase epoxidation rates.[3c] The trend of eq 2 is a specific example involving polarizable alkyl groups. Accordingly, competititions between mono- and disubstituted olefins, di- and trisubstituted olefins, and tri- and tetrasubstituted olefins were performed, and the results are shown in Table VI.

It can be seen that the differences in reactivity between these substitution patterns become attenuated and ultimately lead to a case in which steric effects overcome the electronic effects.

The Transition Structure

A subtle point in the discussions regarding the mechanism of the Prilaschajew reaction deals with the orientation of the approaching olefin with respect to the plane defined by the peracid atoms. Two extremes are defined by the structures below: one in which the C=C bond is parallel to the O–H bond and one wherein these bonds are perpendicular (spiro). The former permits the formation of the second CO bond of the epoxide from the remnants of

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[13] Raber, D. J.; Gariano, P., Jr.; Broad, A. O.; Gariano, A.; Guida, W. C.; Guida, A. R.; Herbst, M. D. *J. Org. Chem.* **1979**, *44*, 1149–1154.

Table III. Relative Reactivities of Tetrasubstituted Olefins

peracid of	12/9	10/11	9/11	10/9
MCPBA	8.5	3.3	1.3	2.2
3a	4.1	6–11	3.2	2.7
3c	2.4	4–8	4.8	2.1

Table IV. Cis/Trans Selectivities for Epoxidations

	k_{cis}/k_{trans}			
peracid of	2-octenes	*t*-BuC(H)=C(H)Et	cyclododecenes	cyclohexene/ methylene-cyclohexane
14 (R = H)	3.8	3.5	0.75	1.7
15a (R = CH_3)	5.6	4.0		2.4
15b (R = CH_2CH_3)	7.7	7.8		3.2
MCPBA	1.2	1.0	0.47	0.84

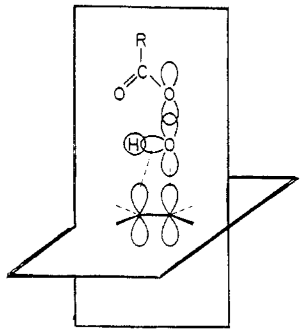
Table V. Steric Effects

peracid of	*cis*-2-octene/*cis*-*t*-BuC(H)=C(H)Et
MCPBA	1.1
14	1.8
15a	2.1
15b	2.2

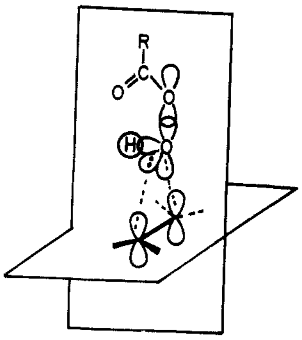
Table VI. Effects of Substitutions

peracid of	2-C_8H_{16}[a]/ 1-$C_{10}H_{20}$[b]	1-MeC_6H_9[c]/ C_6H_{10}[d]	C_9H_{14}[e]/ 1-MeC_6H_9
MCPBA	19.6	13.4	8.7
14 (R = H)	5.6	2.4	1.8
15a (R = CH_3)	4.2	1.9	1.2
15b (R = CH_2CH_3)	3.4	1.6	0.9

the original O–H bond and the LUMO of the olefin, as the proton is transferred.



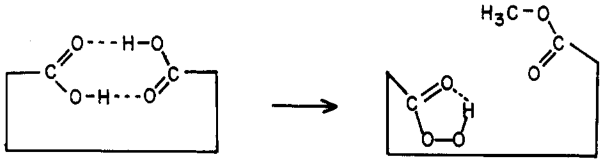
parallel



spiro

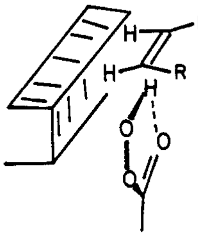
The spiro structure involves one of the lone pairs of the terminal oxygen in bond formation and could lead to a protonated epoxide/carboxylate ion-pair intermediate. This pair would be expected to undergo exothermic proton transfer to products. The spiro structure has been favored in calculations[14] of the reaction and, to the extent that either an intermediate is possible, or a hydrogen bond is maintained, it is supported by studies of primary and secondary isotope effects.[15] A modified version of the spiro structure has also been proposed.[3] Attempts in this department to distinguish between the extremes by ab initio computation at the 3-21G level have been unsuccessful.[16]

The present experimental work does bear on this issue. Structures of the peracids derived from **14** and **15** as defined by either CPK models or molecular mechanics[16] reveal that insufficient space exists between the two carboxyls to accommodate the full complement of the atoms involved in olefin epoxidation. Specifically, replacing the hydrogen-bonded dimer structure **16** by the extra oxygen and the methyl ester in the peracid derived from **15a** can only be accomplished through a twisting motion along the axis of the system as shown schematically in eq 6.



16 **17** (6)

Even with this motion, the terminal oxygen of the peracid becomes directed toward one of the oxygen atoms of the opposing imide function, and it is the limited volume of space between these groups that leads to the observed selectivity. The four representative structures shown maybe used to distinguish between the parallel (C and D) or spiro (E and F) modes for these reagents. If F represents the transition structure, a preference for cis over trans olefins would be hard to rationalize, whereas the parallel approaches C and D explain these differences quite directly. In addition, the spiro mode would favor the epoxidation of methylene cyclohexane over cyclohexene (E and F). In fact, the reverse order is observed, and comparison of C and D illustrates why.



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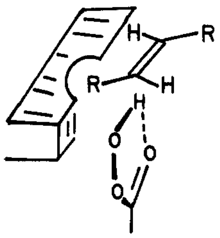

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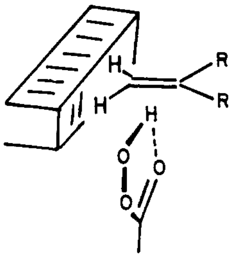

E

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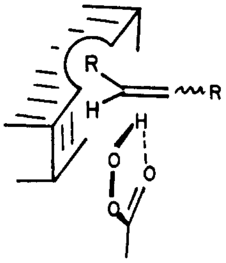

F

It is tempting to generalize from the present results to other peracids, but the special steric constraints that exist in **14** and **15** prejudice the experimental outcome, i.e., their structures disfavor the spiro while they permit the parallel approach. At best, then, this study supports the existence of the parallel transition structure. Whether it is of lower energy than the spiro mode in cases involving conventional peracids will most likely be answered by studies of olefins which present highly structured environments. For ex-

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(14) Plesnicar, B.; Tasevski, M.; Azman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743–746. Bach, R. D.; Willis, C. L.; Domagala, J. M. In "Applications of Molecular Orbital Theory in Organic Chemistry"; Czismadia, I. G., Ed.; Elsevier: Amsterdam, 1977; 221–229. For theoretical studies of other epoxidants see: Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1410–1415; Lang, T. J.; Wolber, G. J.; Bach, R. D. *Ibid.* **1981**, *103*, 3275–3282; Bach, R. D.; Wolber, G. J.; Coddens, B. A. *Ibid.* **1984**, *106*, 6098–6099.

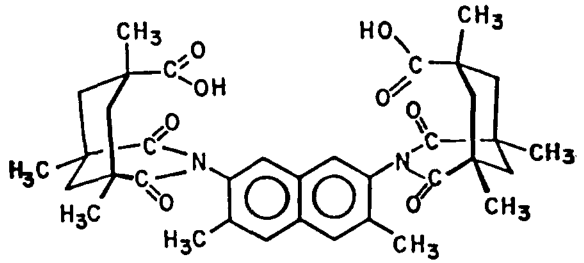
(15) Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231–5233.

(16) Houk, K. N.; Rondan, N., unpublished observations.

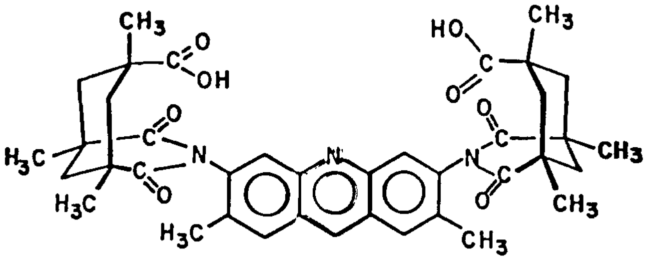
ample, the sesquinorbornene 8 would seem to better accommodate a parallel approach than a perpendicular one; its reported[12] reactivity supports the parallel transition structure, but competition experiments with other tetrasubstituted olefins are necessary to confirm this surmize.[17]

Outlook

Given the distortions in structure that accompany the formation of the peracids **15**, the preparation of chiral derivatives for use in asymmetric epoxidations was not pursued. We have, however, prepared homologues in the form of the naphthalene **18** and acridine **19**. These appear to offer sufficient space between the carboxyls to accommodate an asymmetric center in the region desired. We shall apply these to the Prilaschajew reaction in the future. In the meantime, we note that the reaction selectivity described here may be regarded as a dynamic form of recognition that operates at the stereochemical level. The structures **18** and **19** provide a cleft capable of recognition at a molecular level, and we have made much progress in exploiting them within this context.[18]



18



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Experimental Section

Materials. Experimental details for the preparation of compounds **3**, **14**, and **15** and their derivatives have been described recently;[4b] olefins were commercial samples; **10**,[19] **11**,[20] and **12**[21] were prepared by literature methods. All expoxides are known compounds and standards were prepared by MCPBA epoxidation of the corresponding olefins.

Synthesis of the Acid 4. A modification of the general procedure of ref 4b was used. A solution of 1,8 diaminonaphthalene, 69 mg (.436 mmol), and 112 mg of **5** (.43 mmol) with 61 μL of Et_3N in 3 mL of toluene was heated at reflux overnight under a nitrogen atmosphere. A yellow solid separated from the dark brown solution. The solid was collected by filtration and washed with 10 mL of H_2O. After drying the pale yellow solid weighed 94 mg (60%) and showed mp 318–320 °C after darkening at ~305 °C. NMR (30 MHz, pyridine-d_5): δ 1.24 (d, J = 13.2 Hz, 1 H), 1.32 (s, 3 H), 1.36 (d, J = 13.2 Hz, 1 H), 1.39 (d, J = 13.2 Hz, 1 H), 1.41 (s, 3 H), 1.56 (s, 3 H), 1.94 (dt, J = 13.2 Hz, 2 Hz, 1 H), 3.05 (d, J = 13.2 Hz, 1 H), 3.07 (d, J = 13.2 Hz, 1 H), 7.01 (t, J = 8 Hz, 1 H), 7.18 (d, J = 8 Hz, 1 H), 7.23–7.33 (m, 3 H), 8.45 (d, J = 8 Hz, 1 H). Mass spectrum: m/z 362, 334, 317, 289, 168. High-resolution mass spectrum: 362.1635; calcd for $C_{22}H_{22}N_2O_3$, 362.1630. The corresponding acid chloride was prepared in quantitative yield as a pale yellow solid, mp 146–149, using oxalyl chloride. NMR (30 MHz, $CDCl_3$-pyridine-d_5): δ 1.3-1.5 (axial doublets, 3 H), 1.37 (s, 3 H), 1.39 (s, 3 H), 1.48 (s, 3 H), 2.13 (d, J = 14 Hz, 1 H), 2.84 (d, J = 14 Hz, 1 H), 2.96 (d, J = 14 Hz, 1 H), 7.12 (d, J = 7.2 Hz, 1 H), 7.33 (apparent triplet, J = 7.5 Hz, 1 H), 7.35 (d, J = 7.5 Hz, 1 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.46 (apparent triplet, J = 7.2 Hz, 1 H), 7.98 (d, J = 7.5 Hz, 1 H). Mass spectrum: m/e 382, 380, 316, 273, 168.

Typical Epoxidation Competition Experiments. Standardization. The olefins were purified by passage through a column of silica and checked for purity by gas chromatography prior to use. Solutions (.5–1.0 M) in each of the competing olefins were prepared in 1-mL volumetric flasks using CH_2Cl_2 or $CDCl_3$ solvent. Gas chromatographic analysis (Hewlette-Packard 5710-A instrument) then afforded the exact ratio of olefins in the solution.

Reactions. The appropriate acid chloride (5–10 mg) was weighed into a dry 5-mL screw top vial and to this was added by syringe a volume of the olefin solution such that 5–10 equiv of each olefin were present. The volume was adjusted to 400 μL with solvent when necessary. Pyridine (2–5 μL) was added followed by 5 μL of 90% H_2O_2. The vials were capped and left at room temperature about 1 h. When GC analysis had to be delayed, the samples were stored in the freezer. Gas chromatographic analysis afforded the epoxide ratios which were corrected for any differences in initial olefin concentrations. This value was then reported as the rate ratio. Reproducibility was within 3%. Epoxide yields ranged from 20% (monosubstituted olefins) to 90% (trisubstituted olefins). Attempts to isolate and characterize the actual peracids were unsuccessful.

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Registry No. **3a**, 99309-16-7; **3b**, 99309-17-8; **3c**, 101316-40-9; **4**, 101349-70-6; **9**, 1674-10-8; **10**, 5749-72-4; **11**, 493-03-8; **12**, 4233-18-5; 14, 88730-28-3; **15a** (R = Me), 101316-41-0; **15b** (R = Et), 101316-42-1; MCPBA, 937-14-4; (Z)-MeCH=CHC_5H_{11}, 7642-04-8; (E)-MeCH=CHC_5H_{11}, 13389-42-9; (E)-*t*-BuCh=CHEt, 690-93-7; (Z)-*t*-BuCH=CHEt, 690-92-6; $PhC(CH_3)=CH_2$, 300-57-2; (E)-PhCH=$CHCH_3$, 873-66-5; $CH_2=CHCH_2C_7H_{15}$, 872-05-9; (Z)-cyclododecene, 1129-89-1; (E)-cyclododecene, 1486-75-5; cyclohexene, 110-83-8; methylenecyclohexane, 1192-37-6; 1-methylcyclohexene, 591-49-1; 2,3,4,5,6,7-hexahydro-1*H*-indene, 695-90-9.

Supplementary Material Available: Tables of GC parameters for cis/trans pairs, for 1,1- and 1,2-disubstituted olefin pairs, and for other olefin pairs and GC parameters and retention times for tetrasubstituted olefins (2 pages). Ordering information is given on any current masthead page.

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