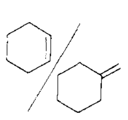
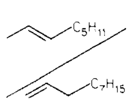
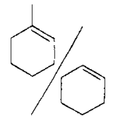
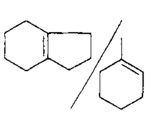
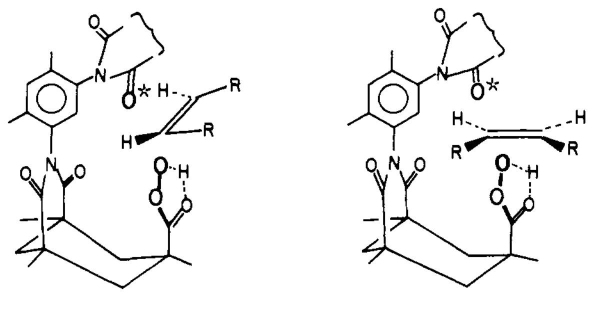
Table I. Epoxidation Selectivities for Peracids (25 °C)

olefin pair + reagent[a]	2-octenes k_{cis}/k_{trans}	HC(t-Bu)=C(H)Et k_{cis}/k_{trans}				
m-$ClC_6H_4COCl + H_2O_2$	1.2	0.96	0.84	19.6	13.4	8.7
4a + H_2O_2	3.8	3.5	1.7	5.6	2.4	1.8
4b + H_2O_2	5.6	4.0	2.4	4.2	1.9	1.2
4c + H_2O_2	7.7	7.8	3.2	3.4	1.6	0.92

[a] Average of three determinations; yields ranged between 20% and 70%.



parallel A spiro B

Figure 1.

increases, the selectivity for cis olefins increases at the expense of trans and 1,1-disubstituted olefins (cyclohexene vs. methylenecyclohexane). The last three columns of the table show that steric effects begin to compete with inductive effects, leading ultimately to retroselectivity, i.e., a case where a trisubstituted alkene reacts *faster* than a tetrasubstituted one.

As a dividend, the trends seen in the table permit some comment on the subtleties of the transition structure for epoxidation. Earlier calculations[6] could not distinguish between the spiro mode B (Figure 1), where the plane of the peracid bisects the C=C bond, to the alternative extreme, A, where this plane is parallel to the C=C bond. More recent calculations, at the most sophisticated levels are also unable to select between these alternatives.[8] An intermediate orientation has also been proposed.[7]

In derivatives **4**, congestion in the area between the carboxyl functions can be relieved by twisting about the C_{aryl}–N bonds in a conrotatory sense.[9] This places an imide oxygen (*) above the peracid function and orients the olefin during the oxygen transfer step.

The preference for cis disubstituted olefins rather than trans is hard to rationalize in a spiro mode (B) whereas the parallel configuration (A) accommodates the facts quite nicely. Likewise, the selectivity for cyclohexene vs. methylenecyclohexane is readily visualized in terms of A over B.[10] While it may be unwise to generalize to conventional peracids from these systems, at least the *existence* of a parallel arrangement is provided by the cases at hand.

We are presently exploring the scope of epoxidations with these reagents and anticipate that asymmetric reactions can be achieved with suitable derivatives.

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(6) Plesnicar, B.; Tasevski, M.; Azman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743–746.

(7) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63–73.

(8) Houk, K. N.; Rondan, N. G., unpublished observations.

(9) Crystallographic studies on derivatives of **3** have been performed by Dr. F. Campagna of the Nicolet Corp.; these reveal that the atoms in the imide and carboxyl functions lie in nearly parallel planes as shown in the figure.

(10) For a most recent study of epoxidation with porphyrin derivatives, see: Groves, J. T.; Nemo, T. G. *J. Am. Chem. Soc.* **1983**, *105*, 5786–5791. Groves, J. T.; Myers, R. S. *Ibid.* **1983**, *105*, 5791–5796.

Additions and Corrections

The First Triple-Decker Sandwich with a Bridging Benzene Ring [*J. Am. Chem. Soc.* **1983**, *105*, 5479]. ALAN W. DUFF, KLAUS JONAS,* RICHARD GODDARD, HANS-JURGEN KRAUS, and CARL KRUGER*

Page 5480, Registry No. paragraph: An incorrect Registry Number was published for $CpCp^{Me}V$ (**10**, Cp^{Me} = 1,2,3,4,5-pentamethylcyclopentadienyl). The correct number is 88271-58-3.