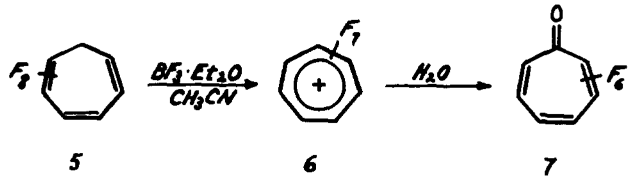
remarkable by contrast with the thermal behavior of the parent quadricyclane, which proceeds quantitatively to a different product, norbornadiene, and requires far more vigorous conditions ($t_{1/2}$ = 3.9 h at 154 °C).[5,11] Thermolysis of the hydrocarbon counterpart[12] of **2** has not yet been studied. Substitution of fluorine for hydrogen on a cyclopropane ring increases ring strain in increments of roughly 5 kcal/mol per fluorine according to O'Neal and Benson.[13] On this basis perfluoroquadricyclane should suffer ≈30 kcal/mol and tricycloheptene **2** ≈15 kcal/mol more strain than the parent hydrocarbons. This extra energy incorporated into skeletons that are already highly strained is probably the key to their extraordinary lability.[14] Perfluorinated carbon skeletons comprising cyclopropane rings fused to other small rings are virtually unknown; our results suggest that such molecules as a class will be highly reactive.

Perfluoronorbornadiene (**1**) fragmented cleanly to perfluorobenzene with loss of difluorocarbene at 240 °C ($t_{1/2} \simeq$ 30 min). The reaction was expected,[15] but the vigor of the conditions required to effect this orbital-topology-allowed, lienar cheletropic elimination[16] is noteworthy. Perfluorocyclopropane extrudes difluorocarbene at temperatures above 160 °C without aromatization as a driving force.[17] The juxtaposition of these two fragmentations highlights once again the large strain energy content of highly fluorinated cyclopropanes.

Tropilidene **5** reacted readily with boron trifluoride etherate in acetonitrile to yield a species whose ^{19}F spectrum was a sharp singlet at δ 99.5. That this species was the perfluorotropylium ion (**6**)[18] was confirmed by its immediate hydrolysis to the known perfluorotropone (**7**)[7,19] by small amounts of water. The ^{19}F NMR spectrum of the tropone (CH_3CN) comprised multiplets of equal area at δ 128.6, 138.2, and 143.8. IR ($CDCl_3$) 1655, 1627, 1535, 1525, 1436, 1385, 1365, 1270, 983 cm^{-1}; MS, *m/e* 214 (M^+).



5 **6** **7**

Further studies relating to the perfluorotropylium ion are under way, including alternative synthetic approaches, isolation of tropylium salts, and exploration of their reactivity.

Acknowledgment. The National Science Foundation (CHE-7924309) and the Air Force Office of Scientific Research (AFOSR-83-0047) have provided generous financial support for this work.

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[10] For a review of the di-π-methane rearrangement, see: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131–166.

[11] Frey, H. M. *J. Chem. Soc.* **1964**, 365–367.

[12] Story, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 3347–3349. Franzus, B.; Synder, E. I. *Ibid.* **1963**, *85*, 3902–3903. Brown, H. C.; Bell, H. M. *Ibid.* **1963**, *85*, 2324.

[13] O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866–1887.

[14] Dolbier has studied extensively the labilizing influence of geminal fluorines on cyclopropane derivatives. Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195–200.

[15] The much more difficult extrusion of :CH_2 does not occur in the pyrolysis of norbornadiene, which yields tropilidene, cyclopentadiene, acetylene, and toluene. Herndon, W. C.; Lowry, L. L. *J. Am. Chem. Soc.* **1964**, *86*, 1922–1926 and references contained therein.

[16] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–932.

[17] The decomposition is very slow at 160 °C, but even an unrealistically conservative extrapolation (assuming $\Delta S^{*} = 0$) to 240 °C indicates faster reaction for the cyclopropane than for **1**. Birchall, J. M.; Haszeldine, R. N.; Roberts, D. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1071–1078.

[18] The chemical shift is at quite low field for vinyl fluorine but is consistent with the strong deshielding observed in other fluorocarbenium ions. Perfluorocyclopropenium ion, for example, gives rise to a singlet at δ 63.1 (in sulfur dioxide, referenced to external trichlorofluoromethane). Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415–419.

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Epoxidations with Selective Peracids

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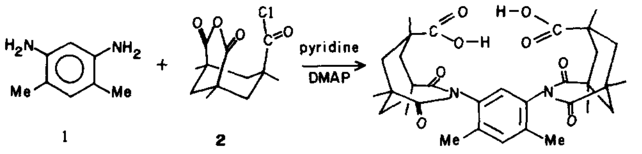
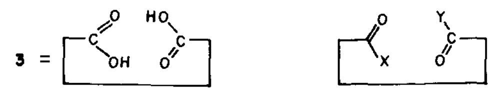
The reaction of peracids with olefins continues to be a general and reliable method of epoxide synthesis. One reason for its consistency lies in the reaction's insensitivity to steric effects, a feature that leads to the familiar sequence[1] of reactivity shown below. An unfortunate corollary is that cis, trans, and 1,1-disubstituted olefins react at nearly the same rate, as do both faces of a given alkene. Consequently, cis/trans and enantioselectivity with conventional peracids is poor. Only with allylic alcohols, where preassociation between olefin and epoxidizing agent is possible, can such selectivity be seen.[2] Here we introduce the first peracids to show general cis/trans selectivity and present evidence that bears on the transition structure.

Relative Reactivities With Peracids

Condensation of the diamine[3] **1** with 2 equiv of the anhydride acid chloride[4] **2** in hot pyridine containing a catalytic amount of 4-(dimethylamino)pyridine (DMAP) gave the diacid **3**, mp >355 °C in 95% yield.[5] With $SOCl_2$ the diacid gave the dihalide **4a**, mp 297–303 °C (95–100%). Treatment of the diacid with 1 equiv of either $Me_3O^+BF_4^-$ or $Et_3O^+BF_4^-$ in the presence of $EtN(i\text{-}Pr)_2$ in methylene chloride provided the corresponding monoesters (mp 331–333 and 277–278 °C, respectively). The monoesters were easily converted to their acid chlorides **4b** (mp 266–268 °C) and **4c** (mp 233–237 °C) in equally high yield.



1 **2** **3**



4a X = Y = Cl
4b X = OMe, Y = Cl
4c X = OEt, Y = Cl

The corresponding peracids were generated in situ by treating **4** with excess H_2O_2 in $CDCl_3$ or CH_2Cl_2 containing an equivalent of pyridine. The appropriate olefin pairs were present in 5- to 10-fold excess. The peracid of *m*-chlorobenzoic acid was likewise generated as the standard reagent; its selectivity was unchanged from that of crystalline peracid under these conditions. Table I summarizes results of the epoxidations.

It can be seen that as the size of the alkyl group of the ester

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[1] Swern, D. "Organic Peroxides"; Wiley: New York, 1971; Vol. 2, p 355. For a study of cis/trans selectivity, see: Stumpf, W.; Rombusch, K. *Justus Liebigs Ann. Chem.* **1965**, *687*, 136–149.

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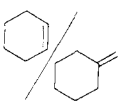
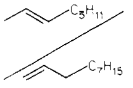
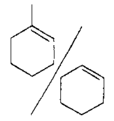
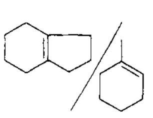
[3] Noelting, E.; Thesmar, G. *Ber.* **1902**, *35*, 628–650.

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

[5] All new compounds were characterized by a full complement of spectra, including high-resolution mass spectra.

0002-7863/84/1506-1170$01.50/0

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%.

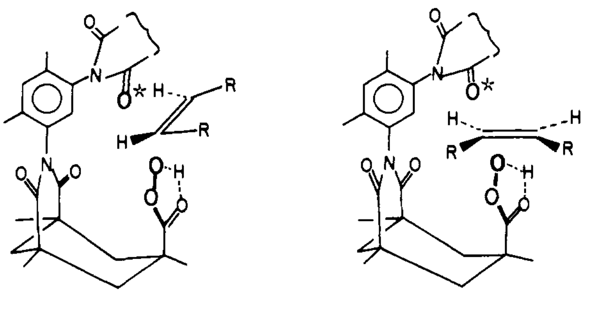

parallel A spiro B

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.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research, to Professor K. N. Houk for advice, and to Professor D. S. Kemp for helpful correspondence.

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(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.