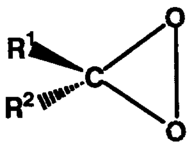
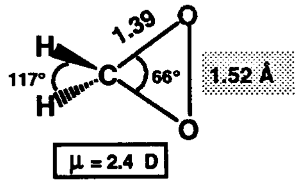
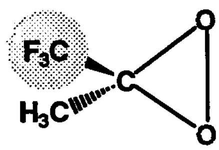
Dioxiranes: a New Class of Powerful O-atom Transfer Agents

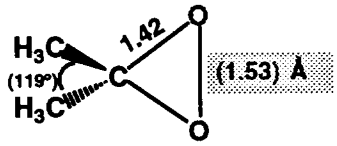




From gas phase MW Spectra
Suenram, Lovas *JACS* **1978**, 5117



TFD



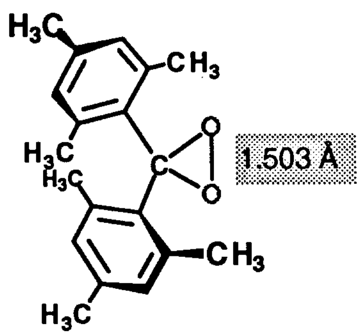
DMD

Theor. Calcns
Cremer, Schindler, *Chem.Phys.Lett.* **1987**, 293

Cf., O-O bond common peroxides 1.44-1.50 Å

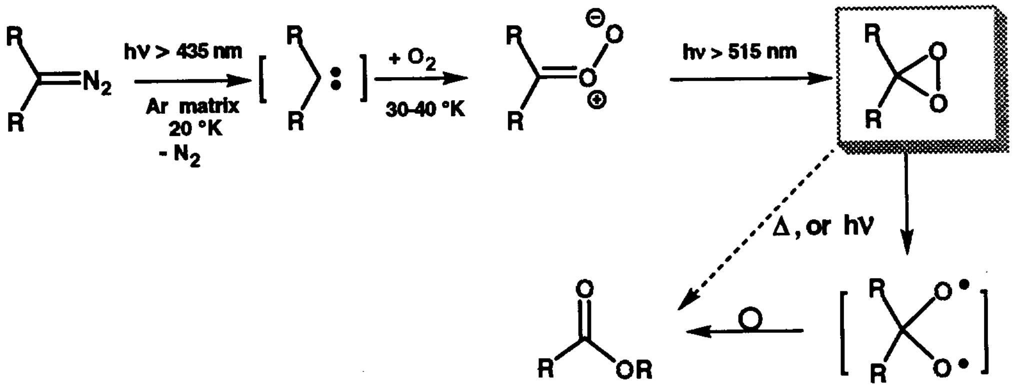
Isolated by synthesis in matrices, organic glasses, or solution

Dimesityldioxirane
mp 62-64 °C
separated by HPLC
yield 50-60%
X-ray crystal structure



Sander et al., *JACS* **1997**, 7265

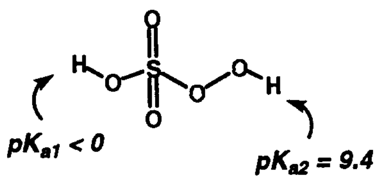
Carbonyl Oxides and Dioxiranes from Oxygenation of Carbenes in Argon Matrices



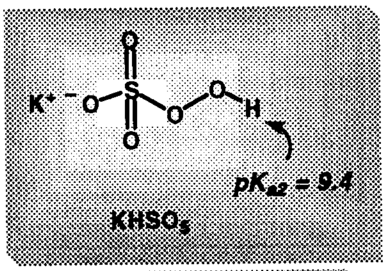
Sander et al., *JACS* **1997**, 7265

Potassium caroate: an inexpensive inorganic peracid

Peroxymonosulfuric Acid
(Caro's Acid)



Potassium Peroxymonosulfate
(Potassium Caroate)



Industrial price: ca.. $ 4. / kg **Commercial Bleach Triple Salt** **2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$**

OXONE®(DuPont); CAROAT®(Degussa); CUROX®(Peroxide Chemie)

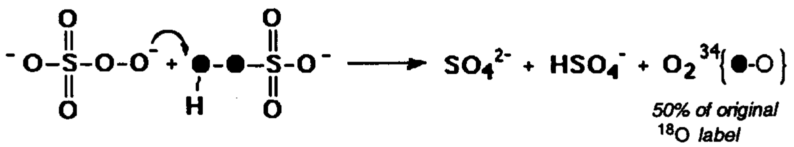
(n-Bu_4N^+)(Oxone) *soluble in CH_2Cl_2* Trost, Braslau *JOC* **1988**, 532.

Uncatalysed "Non-radical" Decomposition of Caroate

Stoich: $2\,HSO_5^-$ ⟶ $2\,SO_4^{2-} + 2\,H^+ + O_2\uparrow$

Rate law: $R = k_2^d\,[HSO_5^-]\,[SO_5^{2-}]$ overall second order in peroxide

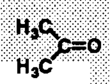
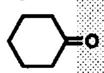
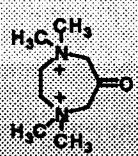
Mechanism:



Edwards, *Inorg.Chim.Acta.Rev.* **1968**, 53 and refs.

Ketone-catalysed Caroate Decomposition

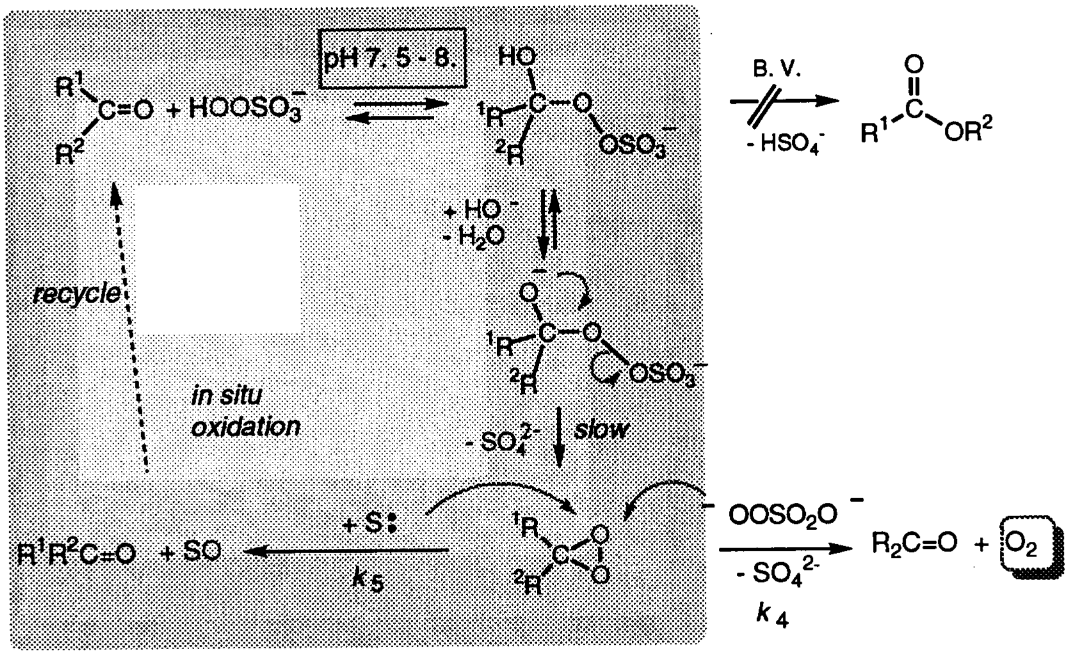
pH 9., at 25 °C

Ketone	Rel. Rate
none	< 0.1
	1.0
	9.4
	1440.
	~ 6000.*

Ketone not consumed and it can be recovered unchanged, unless it has certain structural features (e.g. cyclobutanone).

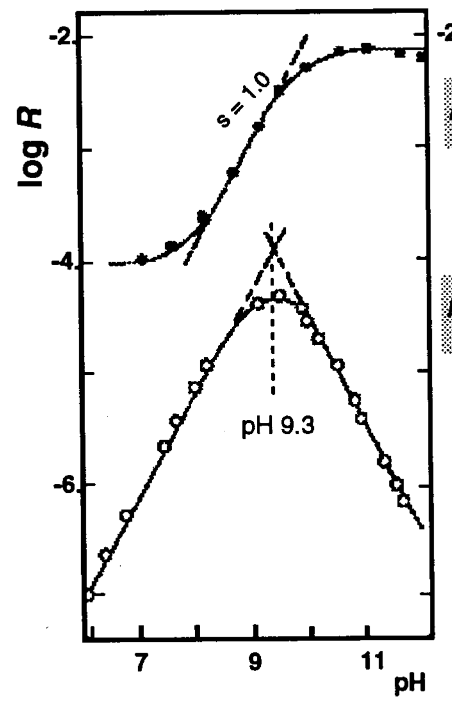
Curci In *Advances in Oxygenated Processes* ; JAI Press: **1990**; Vol. 2, Chapter 1.
Montgomery *JACS* **1974**, 7820
* Newly introduced by Denmark et al.: *JOC* **1998**, 2810

Oxidation of Donor Substrates by Dioxirane *in situ* from Ketone/Caroate



Edwards, Curci et al. *Photochem. Photobiol.* **1979** , 63.
Curci In *Advances in Oxygenated Processes* ; JAI Press: **1990**; Vol. 2, Chapter 1.

Dependence from pH and Rate Law for the Uncatalysed (25 °C) and for the Cyclohexanone-catalysed Caroate Decomposition (28° C).

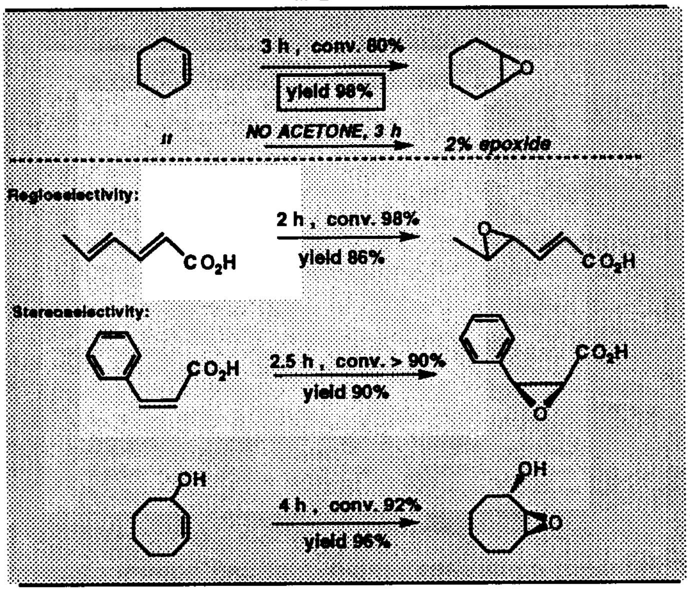


$R = k_2 [HSO_5^-] [\text{ketone}] [HO^-]$

$R = k_2^d [HSO_5^-] [SO_5^{2-}]$

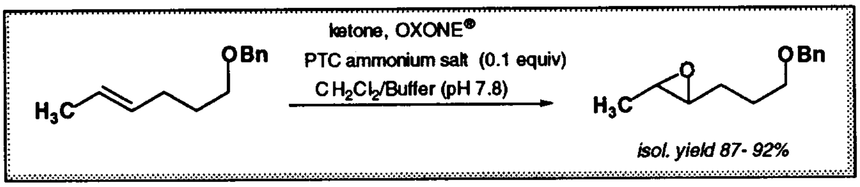
Curci In *Advances in Oxygenated Processes* ; Baumstark, Ed.; JAI : **1990**; Vol. 2, Chapter 1.

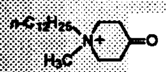
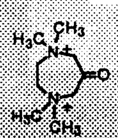
Epoxidations by Dimethyldioxirane *In Situ* (from Acetone and Caroate)
in Water or Water (pH 7. -7.5) / CH_2Cl_2 Biphasic System $Bu_4N^+HSO_4^-$ (PTC),
at 2 - 10 °C



Curci et al. *JOC* **1980**, 4758; **1982**, 2670

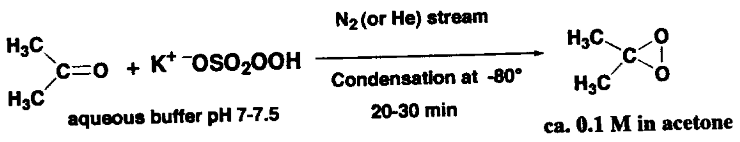
Example of Optimization of Alkene Epoxidation by Dioxirane *In Situ*.
Oxidation for (*E*)-6-(Phenylmethoxy)-2-hexene.
Oxone excess (10 equiv) added during 8 h, at 0° C.



ketone	equiv	epoxide/ olefin ratio	reaction time
acetone, $Bu_4N^+HSO_4^-$	2	87 / 13	24 h
	1	100 / 0	24 h
	0.1	100 / 0	11 h *mixed solvent acetonitrile/water pH 7.0*

Denmark et al. *JOC* **1995**, 1391; *JOC* **1998**, 2810.

The Isolation of Dioxiranes

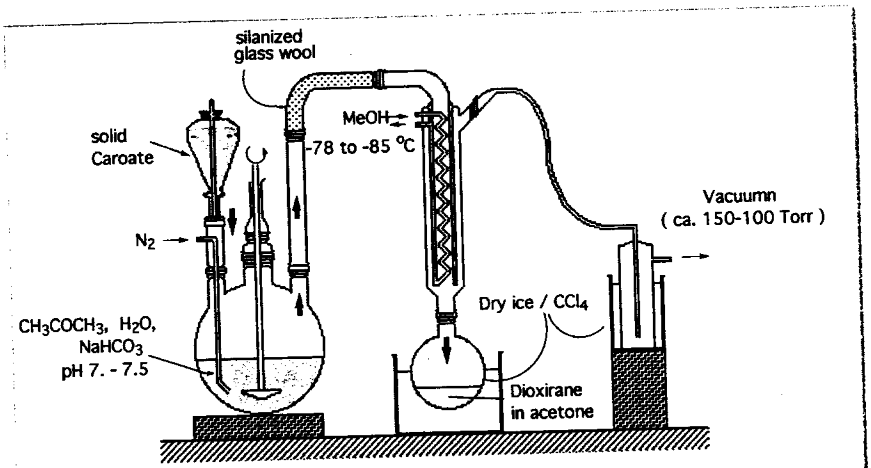


Murray et al., *JOC* **1985**, 2847.

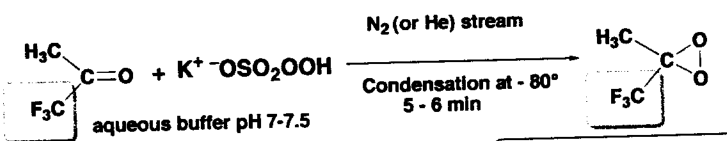
Curci et al., *JOC* **1987**, 699.

λ_{max} = 333 nm (ε ca. 13)
^{1}H NMR: δ 1.65 (s)
^{13}C NMR: δ 22.72 (CH_3)
δ 102.
^{17}O NMR: δ 302. (s)

Apparatus for Isolation of Dioxiranes



The isolation of Methyl(trifluoromethyl)dioxirane



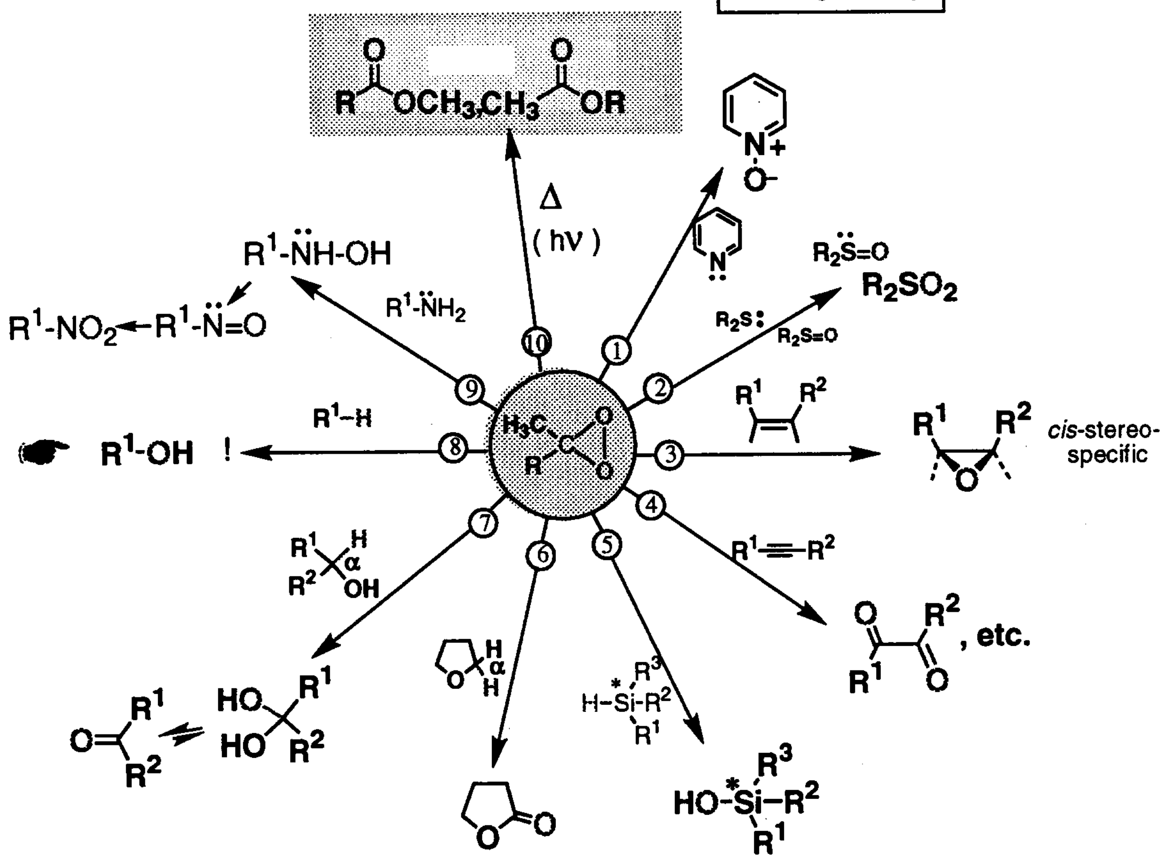
up to 1.5 M in TFP !

Curci et al. *JOC* **1988**, 3890.

λ_{max} = 347 nm (ε ca. 9)
^{1}H NMR: δ 1.97
^{13}C NMR: δ 14.51 (CH_3), 122.2 (CF_3)
δ 97.3
^{17}O NMR: δ 297. (s)

Outline of Dioxirane Reactivity

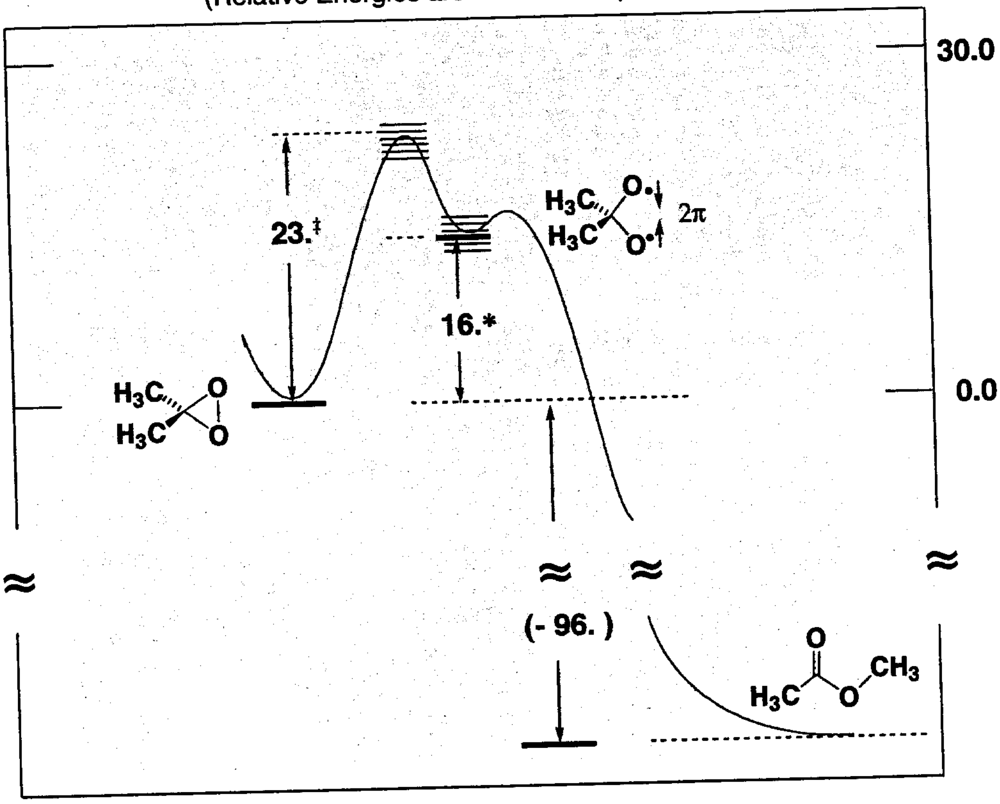
R = CH_3 or CF_3



Most refs., see: (a) Curci et al., *Pure Appl. Chem.* **1995**, 811;
(b)Adam, Hadjiarapoglu, Curci, Mello in *Organic Peroxides*; Wiley: New York, **1992**; Chapter 4.

Energy Diagram for the Interconversion of Dioxirane to Ester via Bisoxymethylene

(Relative Energies are in kcal mol^{-1})

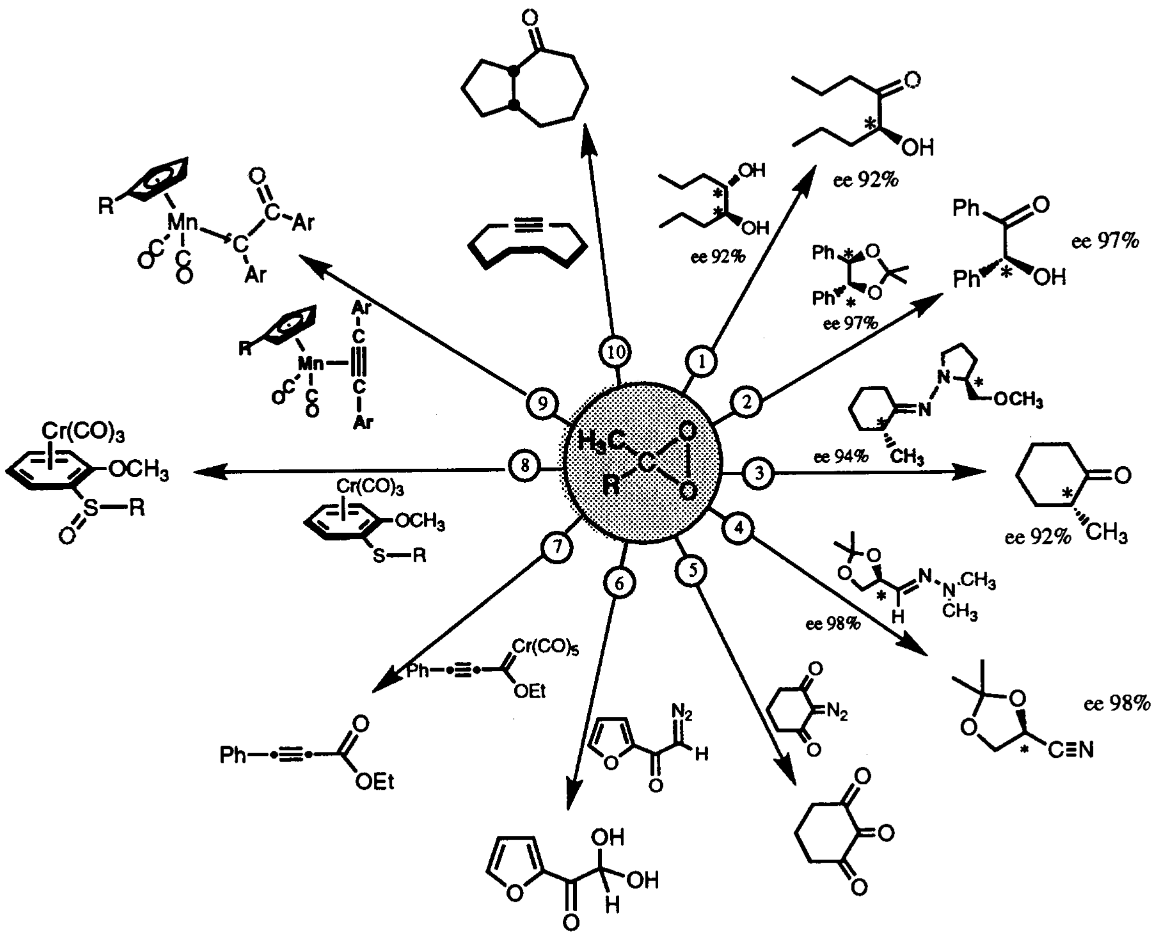


* QCISD(T)/6-311+G(3df,2p)//QCISD/6-31G* : Bach et al., *in press;* see also *JACS* **1992**, 7207.

‡ B3LYP/6-31G(d,p) : Cremer et al. *Chem. Phys. Lett.* **1998**, 97.

Some Transformations Using Dioxiranes

R = CH_3 or CF_3



① Curci et.al. *JOC* **1993**, 3600.

② Curci et.al. *TeLe* **1996**, 115.

③ Curci et al. *JOC* **1993**, 7289

④ Curci et.al. *TeLe* **1998**, 115.

⑤ Saba *Synth. Comm.* **1994**, 695.

⑥ Prato, Scorrano, et.al. *TeLe* **1991**, 6215.

⑦ Messeguer et.al. *TeLe* **1992**, 3021.

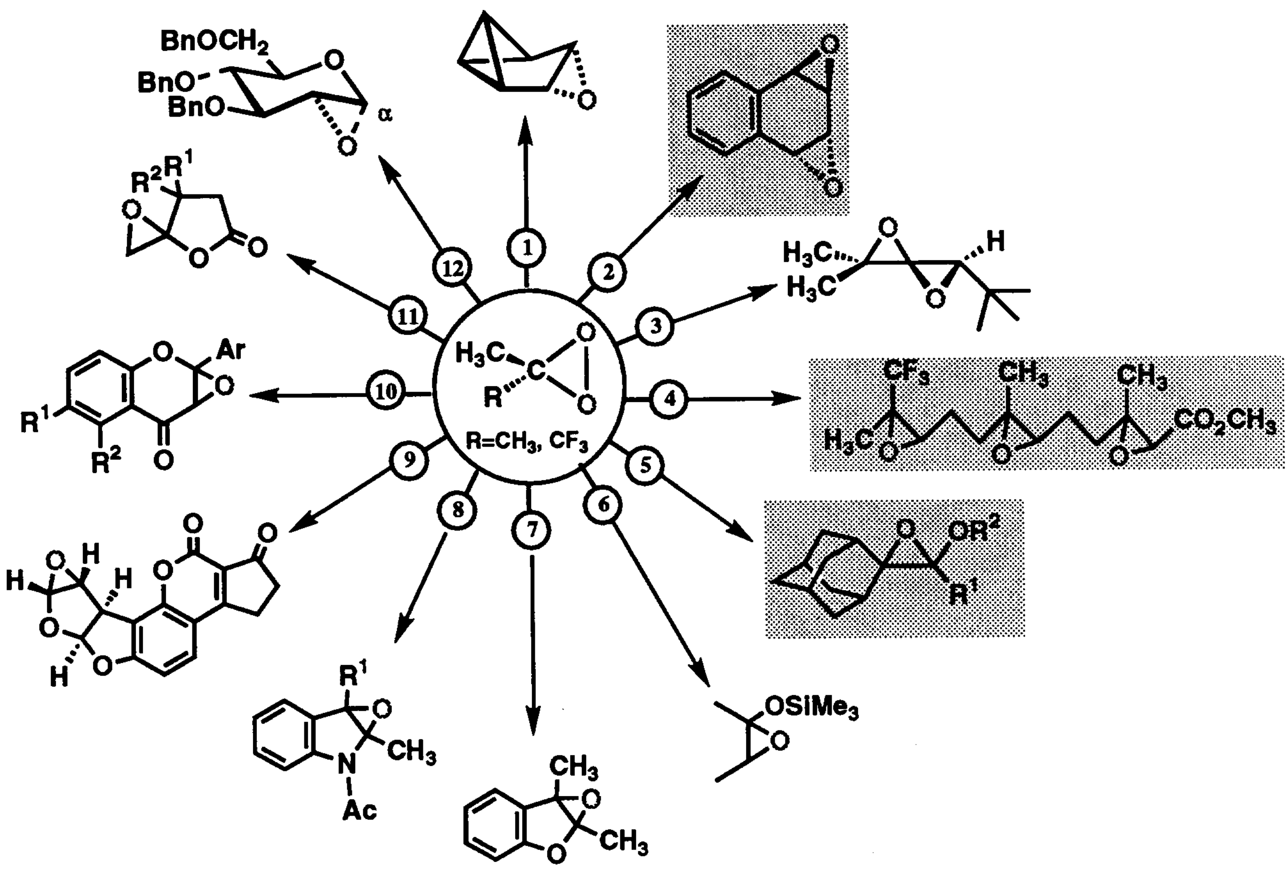
⑧ Thomas et al. *Chem. Comm.* **1993**, 1059.

⑨ Curci, Sweigart et.al. *Organomet. Chem.* **1995**, 1545.

⑩ Curci et.al. *TeLe* **1992**, 7929.

Other examples., see: Adam, Hadjiarapoglu in *Topics Curr. Chem.* **1993**, *164*, 45.

Some Useful Epoxidations Employing Dioxiranes

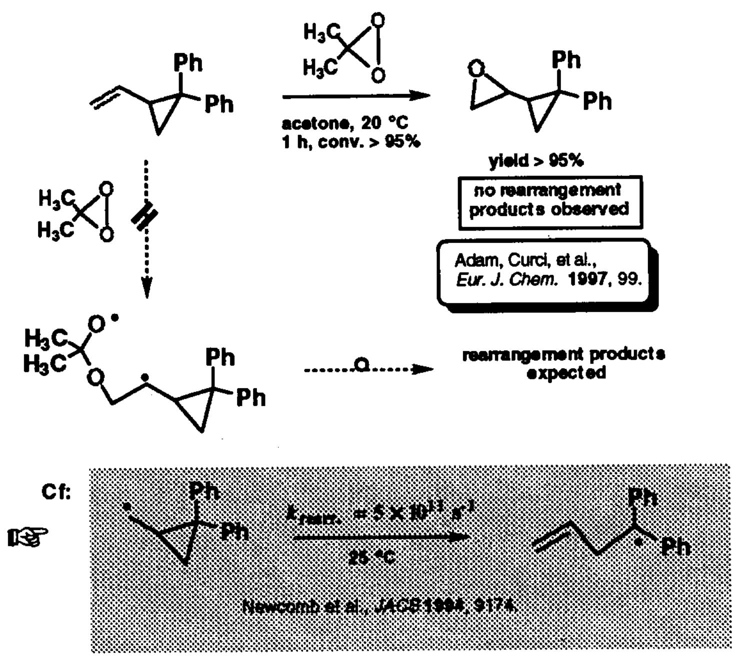


Most Refs., in: Adam, Hadjiarapoglu, Curci, Mello in *Organic Peroxides*; Wiley: New York, 1992; Chapter 4.

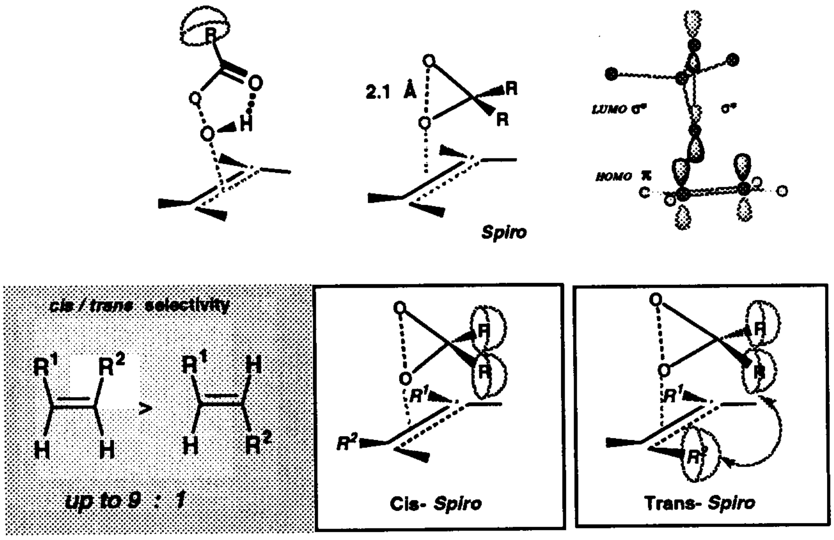
(4) TFD : Curci, Messeguer et al., *Tetrahedron* **1993**, 6299

(8) DMD: Zhang, Foote, *JACS* **1993**, 8867; Adam et al., *JOC* **1994**, 2733.

Application of an Ultra-fast Radical Probe to Dioxirane Epoxidation



Transition state geometries for epoxidations



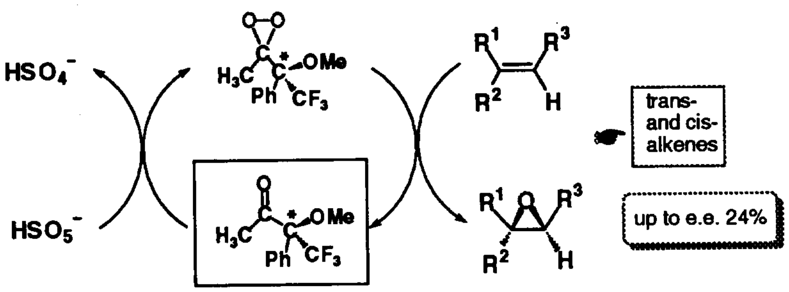
Curci et al., *Pure Appl. Chem.* **1995**, 811.

Recent calculations:

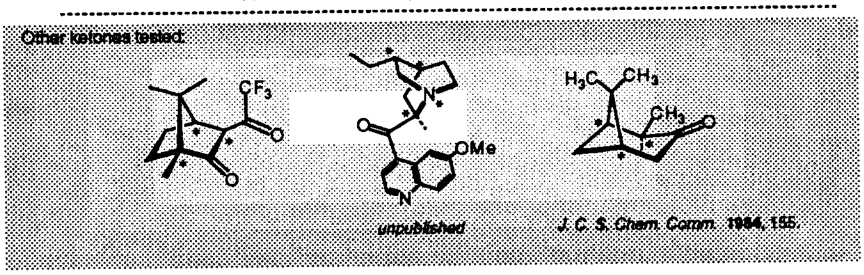
Bach et al., *J. Phys. Chem.* **1997**, 6092.

Houk et al., *JACS* **1997**, 10147.

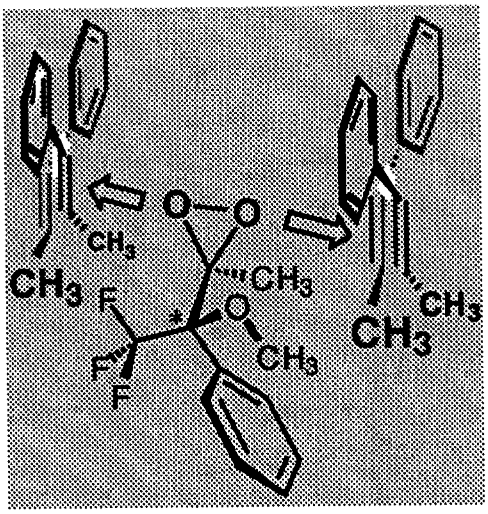
Enantioselective Epoxidations with *In Situ* Dioxiranes



Curci et al. *TeLe* **1995**, 5831.

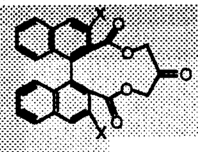
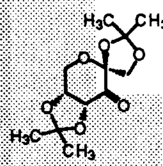


Facial Selectivity and Competing Approaches of an Olefin to Diastereotopic Peroxide Oxygens of Chiral Dioxirane



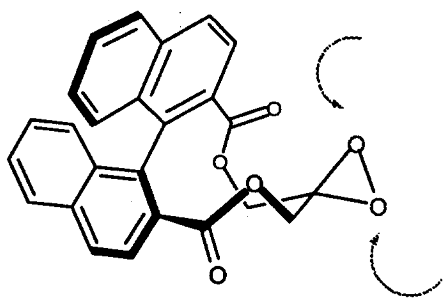
- The α electron-withdrawing groups enhance dioxirane reactivity

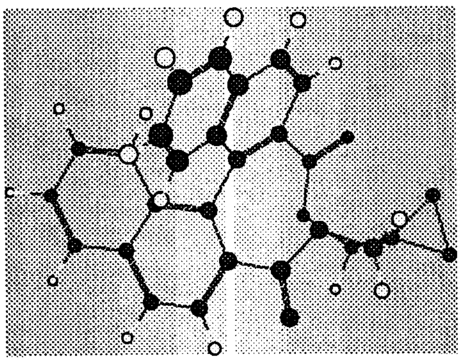
Some examples of Enantioselective Epoxidation
of trans-Stilbene with *in situ* dioxiranes from Ketone and Caroate
in water/organic cosolvent at 20 °C

	Chiral ketone Precursor	Cosolvent	pH	% ee	Note
①		acetonitrile	7.5	47 76	X = H X = Cl
②		acetonitrile/ DMM	10.5	98	but ketone is consumed
③		acetonitrile	7.5	76	X = F

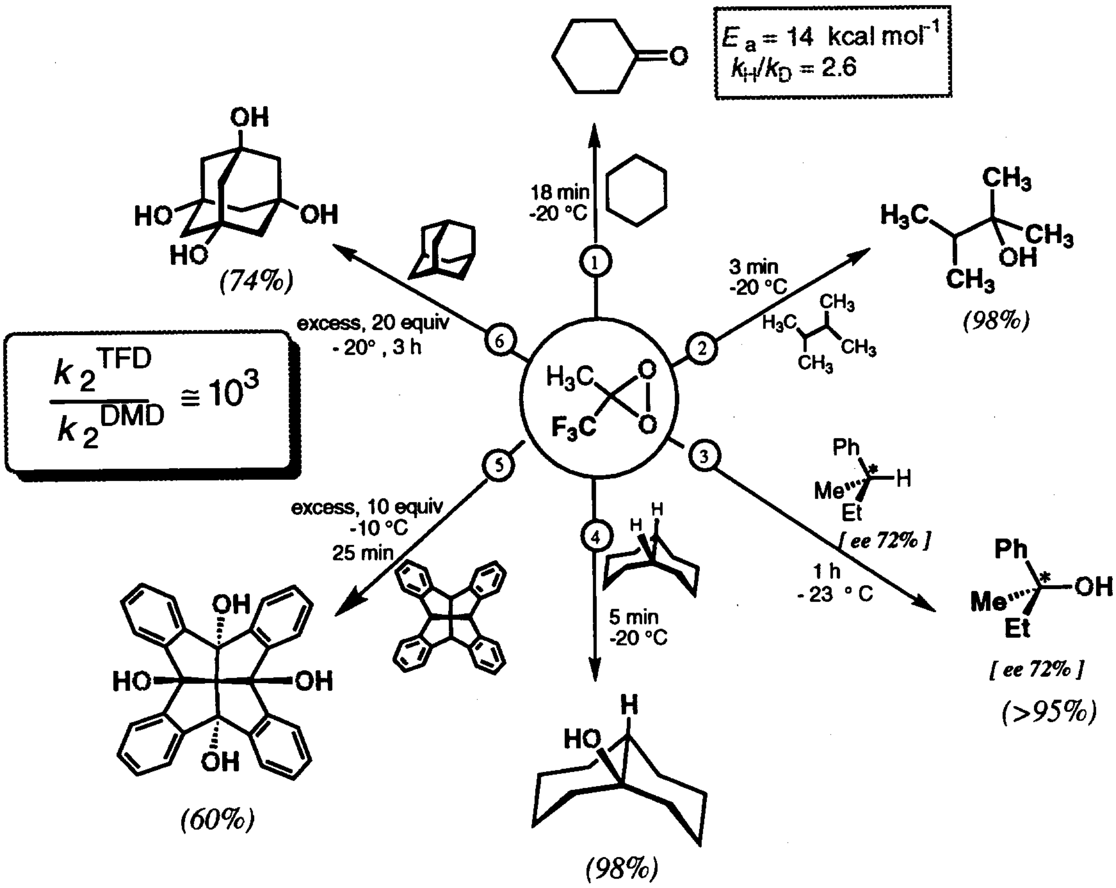
① Yang et al., *JACS* **1996**, 11311. ② Shi et al., *JACS* **1997**, 11224.
③ Armstrong and Hayter, *Chem. Comm* **1998**, 621.
See also: Adam, Zhao, *Tetrahedron Asymm.* **1997**, 3995.

Steric control of competing approaches of olefin achieved by C2 or pseudo-C2-symmetric elements



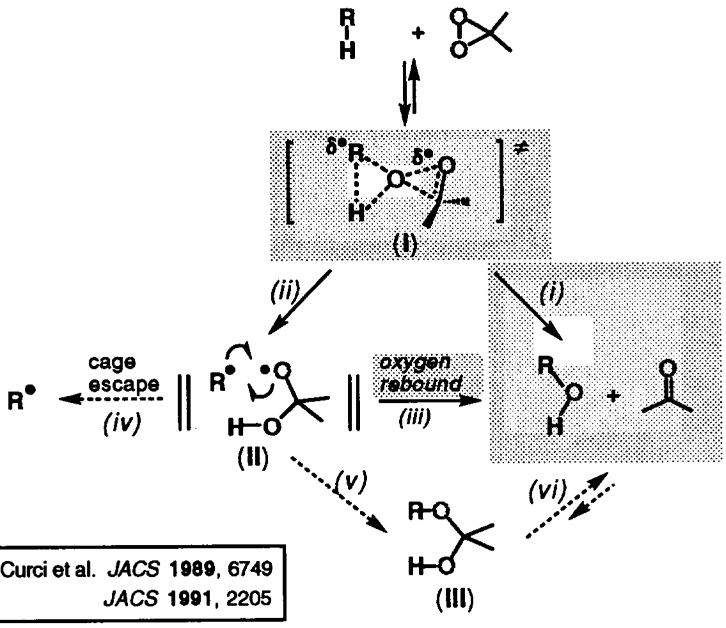


Efficient and highly selective oxyfunctionalization of saturated hydrocarbons using methyl(trifluoromethyl)dioxirane

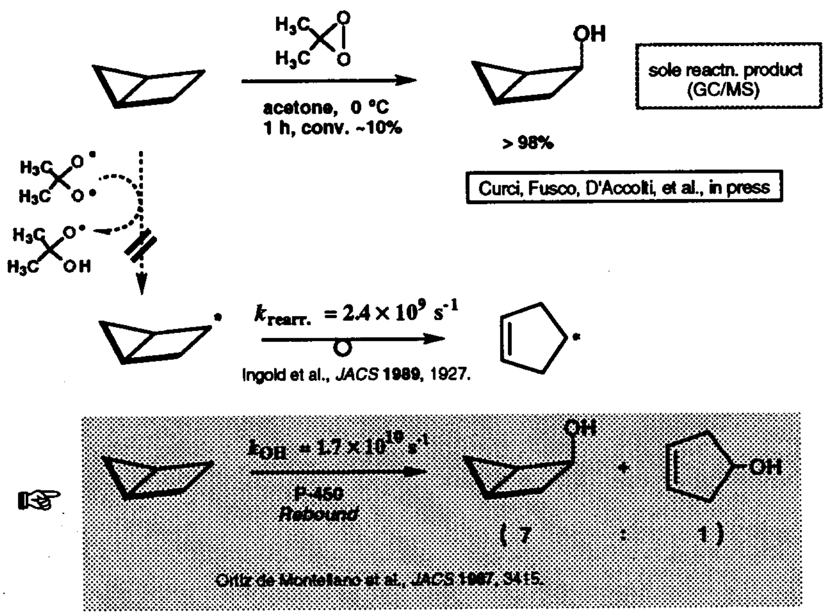


Curci et al. *JACS* **1989**, 6749; *TeLe* **1990**, 3067; *JOC* **1996**, 8681; *Pure Appl. Chem.* **1995**, 811. And refs therein

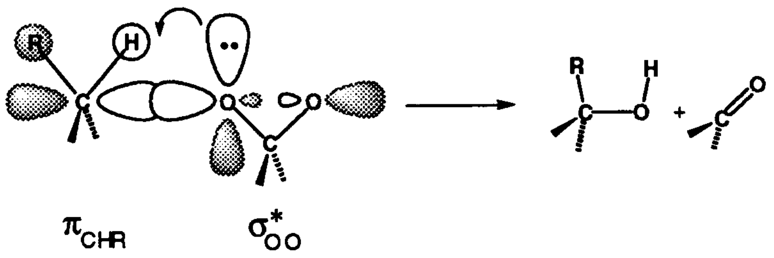
A Likely mechanism of *O*-atom insertion by dioxiranes into C-H bonds of saturated hydrocarbons

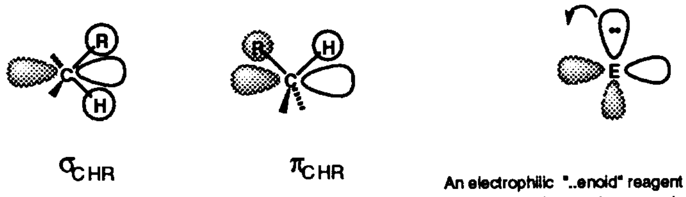


Application of an Ultra-fast Radical Probe to Alkane Hydroxylation by Dioxiranes



FMO for *O*-Insertion by Dioxiranes into C-H bonds



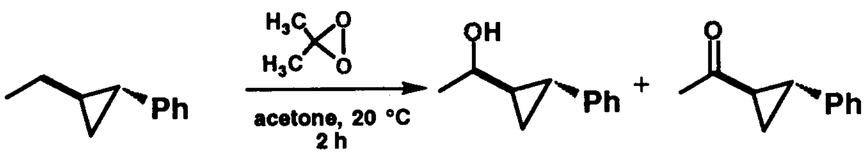


In the description of an hydrocarbon in tetrahedral array <u>no *isolated* MO describe C-H bonds</u>

Bach et al., *JACS* 1992

An electrophilic "..enoid" reagent E capable of insertion into C-H bonds must have an <u>electron deficient orbital</u> to interact with the doubly occupied hydrocarbon fragment orbital <u>and one or more electon pairs</u> that serve as migration terminus for a 1,2-H shift

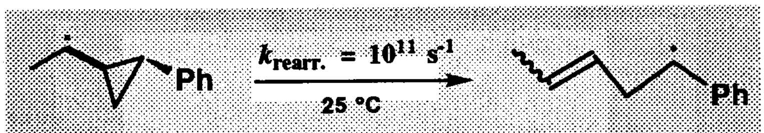
Dioxirane *O*-insertion into C-H of an Ultra-fast Radical Probe



yield > 97%

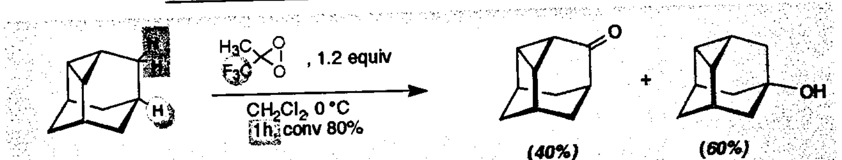
Newcomb et al., *TeLe* **1998**, in press.

Cf:

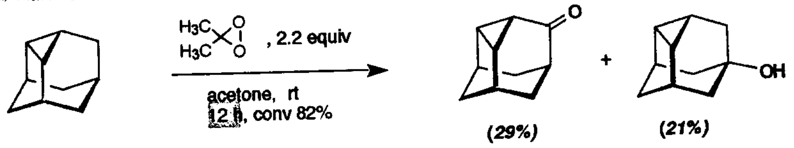


Newcomb et al., *JACS* **1992**, 10915.

Oxidation of 2,4-Didehydroadamantane by Dioxiranes

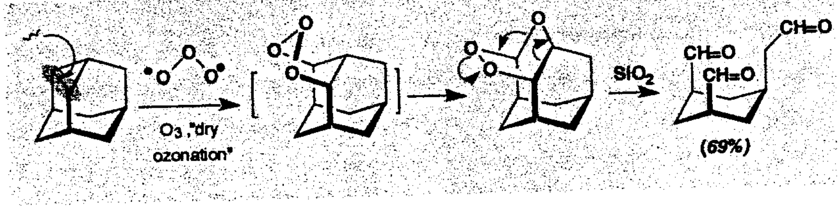


Curci et al. *unpublished*

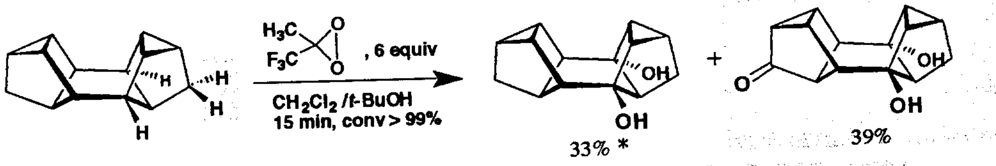


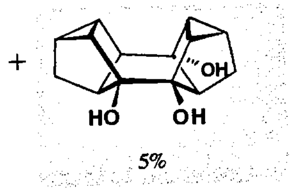
Teager, Murray *JOC* **1993**, 5548

Cf.:



Oxyfunctionalization of Binor S by TFD





Curci, Fusco, D'Accolti *to be published*

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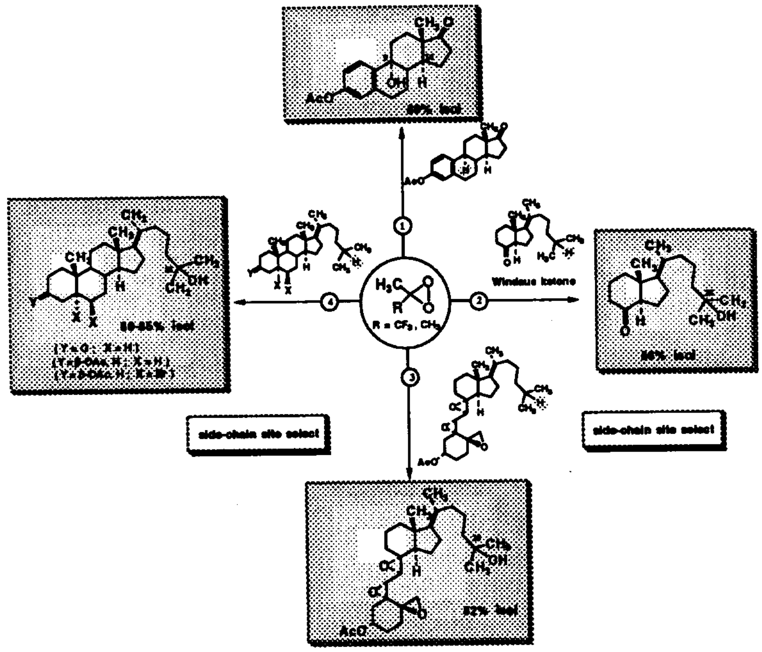
* First isolated by Eaton et al. (*JOC* **1990**, 6105).

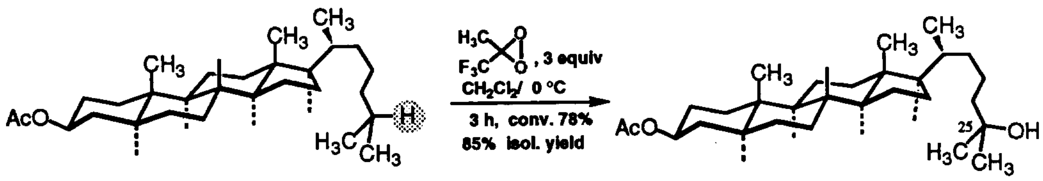
Selected Examples of Selective Oxyfunctionalizations of Natural Targets



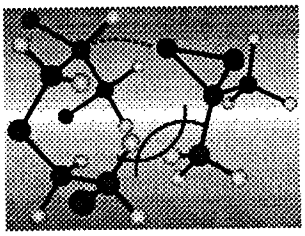
①②④ Curci, Mincione et al., *JOC* **1992**, 2182; *JOC* **1992**, 5052

③ Curci, Detomaso et al., *JACS* **1994**, 8112

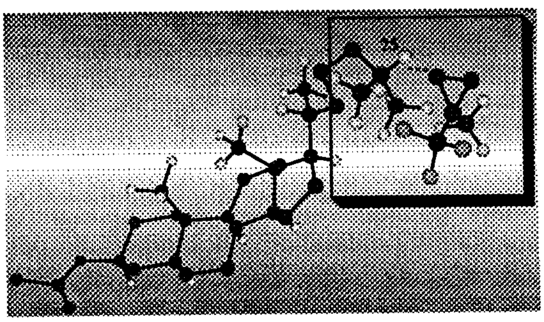
Selective oxyfunctionalization at side-chain C-25



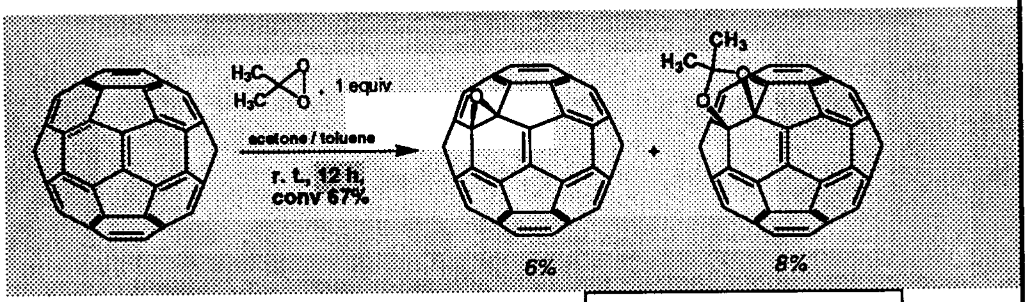
3β-acetoxy-5α-cholestane



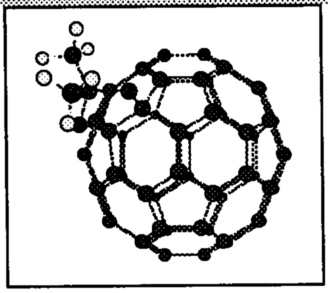
steric hindrance to optimum stereoalignment at tert- C-H



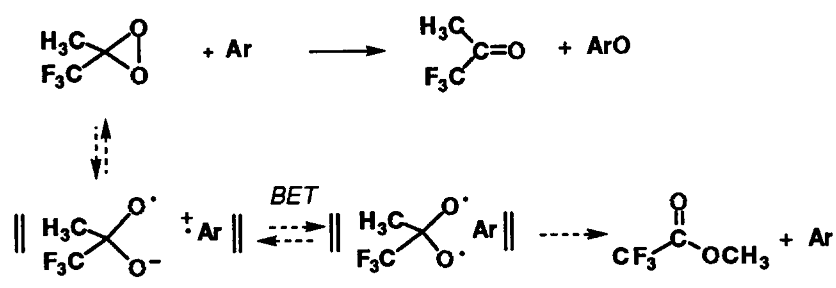
Oxidation of Fullerene C60 by Dimethyldioxirane



Foote et al., *Angew. Chem., Int. Ed. Engl.* **1992**, 351.



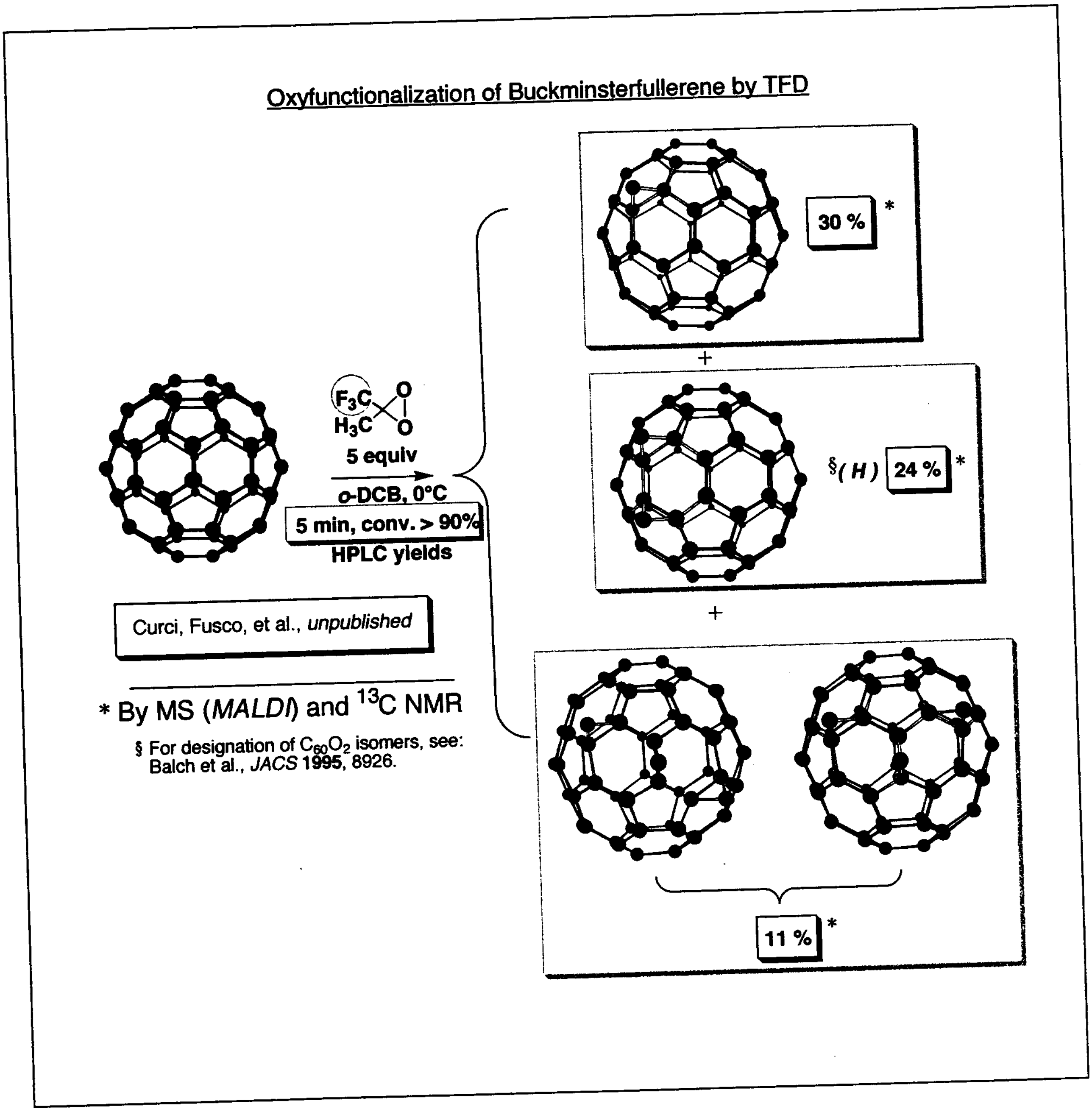
Dioxirane Decomposition During Oxidation of Arenes Having Low Oxidation Potential



Ar = Pyrene, Rubrene

Pyrene$^{+\bullet}$ detected by low-temp ESR

Curci et al., *TeLe* **1990**, 6097.


Oxyfunctionalization of Buckminsterfullerene by TFD
F_3C
H_3C
O
O
5 equiv
o-DCB, 0°C
5 min, conv. > 90%
HPLC yields
30 %*
§(H) 24 %*
11 %*
Curci, Fusco, et al., unpublished
* By MS (MALDI) and ^{13}C NMR
§ For designation of $C_{60}O_2$ isomers, see: Balch et al., JACS 1995, 8926.

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