1

$ROOH + S \longrightarrow ROH + SO$

$R = H$, Alk, Acyl

$S = R_2S$, R_2SO, >C=C<, R_3N, etc

2

$$Nu + H_2O_2 \xrightarrow{Mo,\,V,\,W,\,Ti} NuO + H_2O$$

$$Nu + ROOH \xrightarrow{Mo,\,V,\,W,\,Ti} NuO + ROH$$

$Nu = R_2S$, >C=C< , R_3N etc.

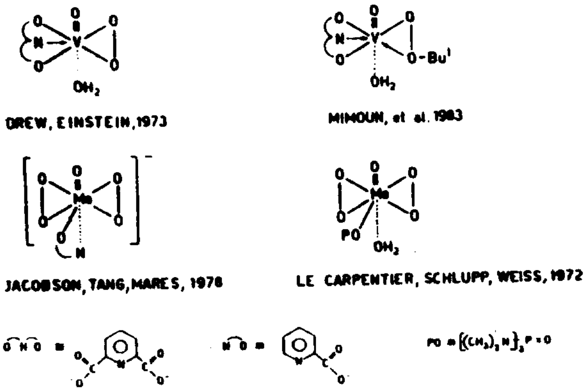
3

$$M + ROOH \rightleftharpoons [M \cdot ROOH]$$

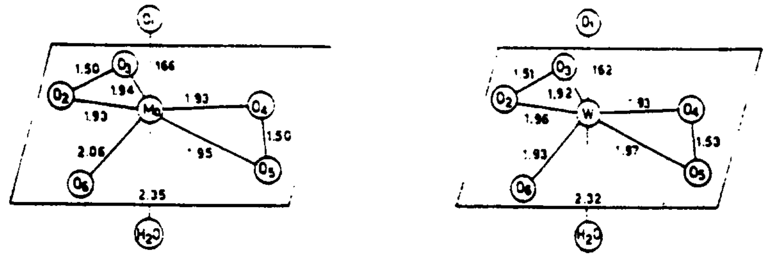
$$[M \cdot ROOH] + S \longrightarrow SO + [M \cdot ROH]$$

$$[M \cdot ROH] + ROOH \rightleftharpoons [M \cdot ROOH] + ROH$$

4

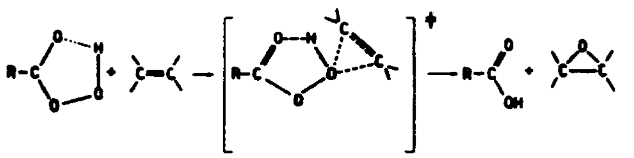


5



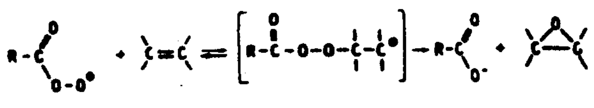
6

Electrophilic oxygen transfer



7

Nucleophilic oxygen transfer



8

	Oxidant			
	RCO_3H	V-TBHP	Mo-TBHP	MoO_5L
	1	$\sim 3 \times 10^{-4}$	$\sim 4 \times 10^{-3}$	$\sim 3 \times 10^{-2}$
Solvent	benzene	benzene	benzene	DCE

RELATIVE RATES AT ~25°

	-S-	-S(=O)-	Solvent
RCO_3H	1	0.3	Dioxane
RCO_3H	1	2×10^{-2}	EtOH-Dioxane 70-30
RCO_3^-	~0	9×10^{-3}	EtOH-Dioxane 70-30
V-TBHP	1	2×10^{-2}	EtOH
Mo-TBHP	1	7×10^{-4}	EtOH
MoO_5	1	1×10^{-2}	EtOH

10

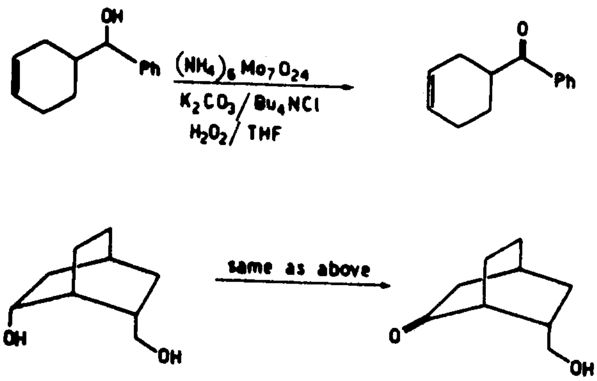
Mo(VI)-CATALYZED OXIDATION OF CYCLOHEXANOL
(Cyclohexanol as solvent)

#	[BASE]/[Mo(VI)]	$-d[H_2O_2]/dt$	$d[C=O]/dt$
1	0	2.7	7.5
2	1	52.8	69.7
3	2	50.8	49.9
4 (in CH_3CN)[a]	0	3.7	41.5[b]

Mo(VI) = $MoO_2(acac)_2$, $1 \cdot 10^{-4}$ M ; H_2O_2 = $4.5 \cdot 10^{-3}$ M ; BASE = $cC_6H_{11}O^-Na^+$

a- Cyclohexanol 1 M in CH_3CN ; b - initial rate

11



(88 %)

(88 %)

OXIDATION OF ALCOHOLS UNDER PHASE-TRANSFER CONDITIONS AT 75°C

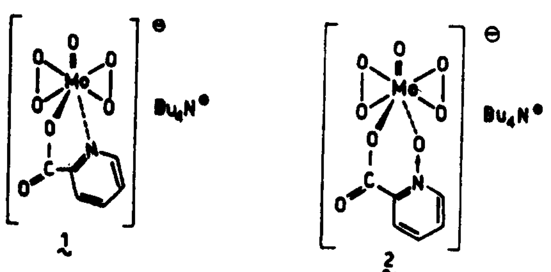
12

Alcohol	Catalyst	t(min)	Product (yield %)
Cyclohexanol	Mo	150	Cyclohexanone (88)
"	W	50	" (~95)
Menthol	Mo	210	Menthone (~96)
"	W	120	" (89)
Borneol	Mo	120	Bornenone (~95)
"	W	45	" (~95)
2-octanol	W	75	2-octanone (~95)
Benzyl alcohol	W	30	Benzaldehyde (85)

DCE (10 ml)- water (1 ml), pH = 3 (Mo), 1.4 (W)

Substrate : H_2O_2 : catalyst : Aliquat 336 = 1 : (2-6) : 0.1 : 0.5

13

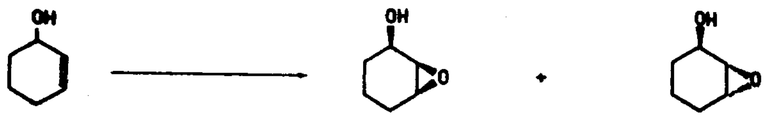


1   2

Cyclohexanol M	Oxidant	10^4 k_1, S^{-1}	Solvent DCE
1.2	1	0.52	
0.4	2	45.0	

Allylic Alcohols

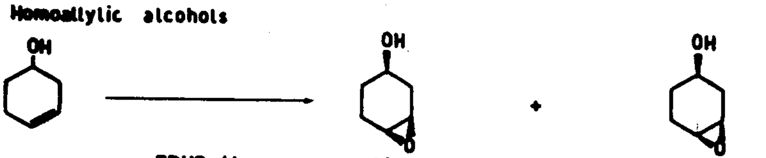
14



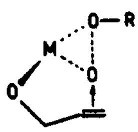
TBHP - Mo	98	2
TBHP - V	98	2
PBA	92	8

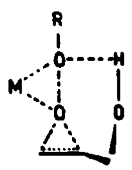
15

Homoallylic alcohols



TBHP - Mo	98	2
TBHP - V	98	2
PBA	60	40

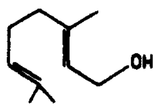
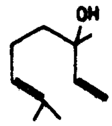




18

	Mo-TBHP		Mo - H_2O_2	
	E_A (Kcal/mol)	log A	E_A (Kcal/mol)	log A
R_2S	15.7	15.4	12.9	12.8
	20.4	14.9	18.8	14.2
	28.1	20.2	17.3	13.3

17

	Geraniol 	Linalool 
	2 : 6	1 : 6
V-TBHP	99 : >1	99 : >1
MoO_5	99 : >1	>1 : 99

19

ENANTIOSELECTIVITY

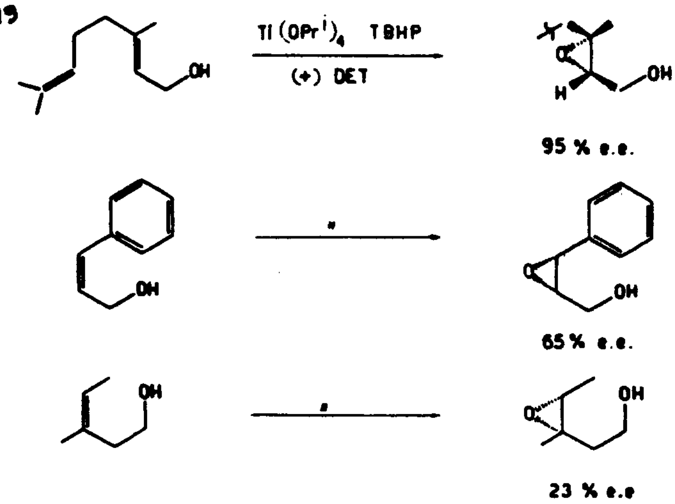
a) CHIRAL REAGENT (chemical or biochemical)

b) CHIRAL SUBSTRATE

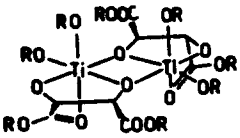
SUBSTRATE DISCRIMINATION ABILITY

Allylic alcohols > Alkenes ~ Sulfides

19



20



R = iPr.

21

$$R_1-S-R_2 \; + \; \xrightarrow[(+)\,DET]{Ti\,(OPr^i)_4} \; R_1-\overset{O}{\overset{\|}{S}}-R_2$$

e.e. 30 - 90 %

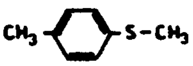
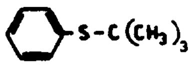
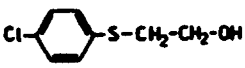
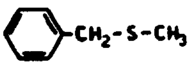
e.e. max. R_1 = CH_3 ; R_2 = p-CH_3 

Ti (IV) : TBPH : (+) DET : H_2O

1 : 2 : 4 : ~0

1 : 1.1 2 : 1

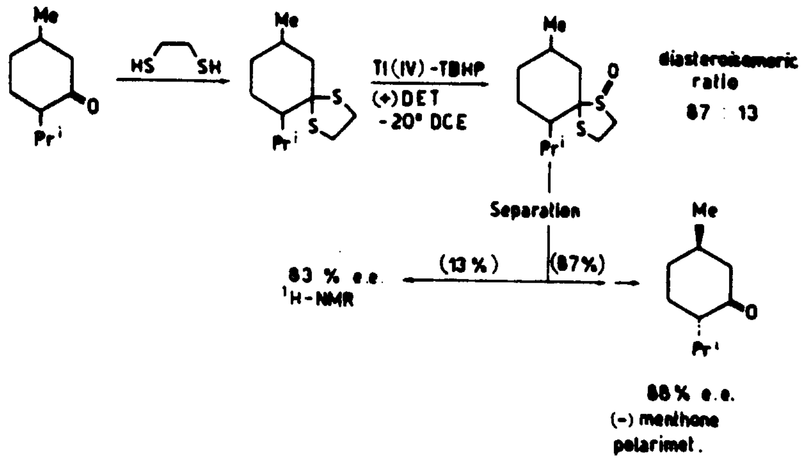
22

Substrate	Solvent	T °C	e.e. %
	DCE	-20	88
	Toluene	-20	35
	Toluene	-20	14
	DCE	-77	46

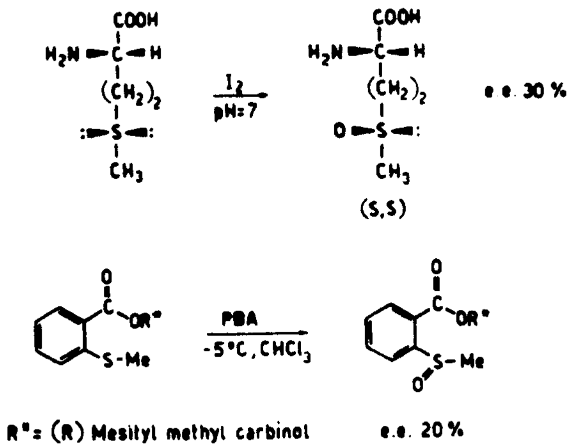
Ph

ca

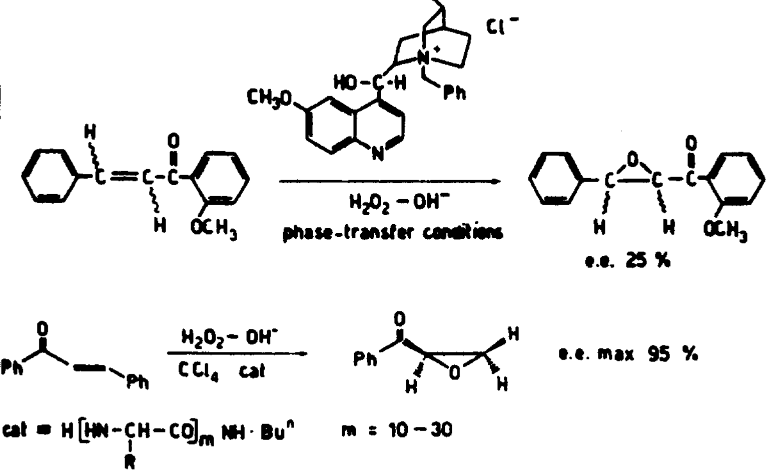
23



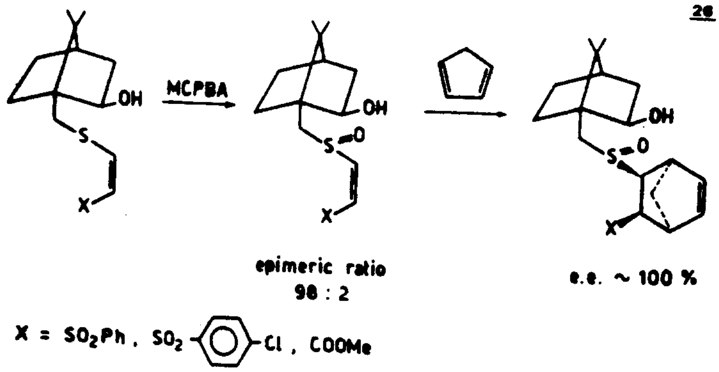
25



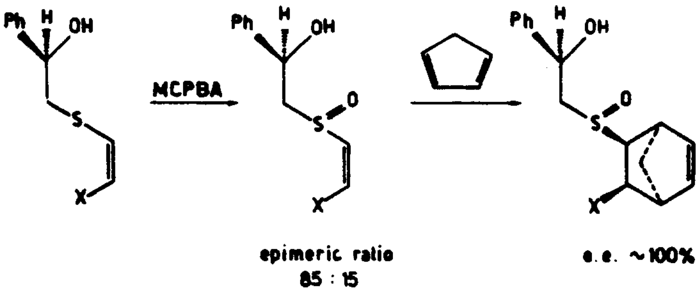
24



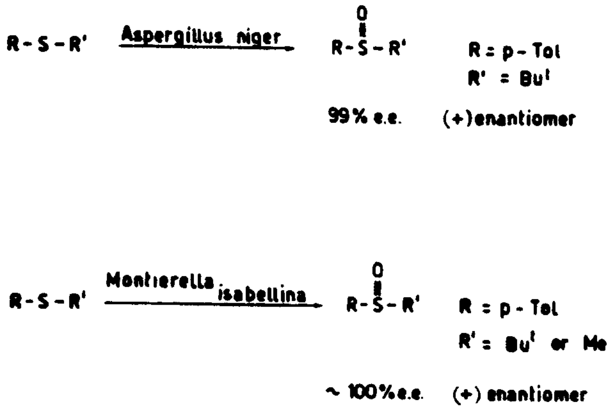
26



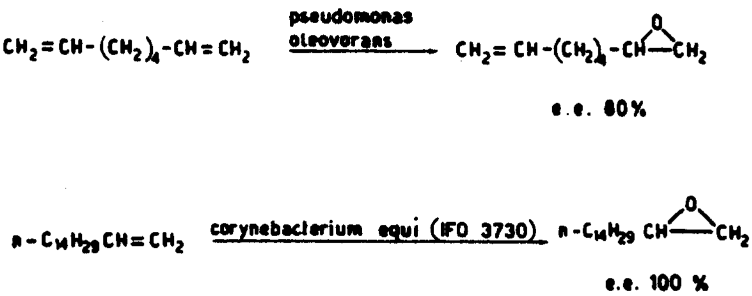
27



28



29



REFERENCES

Slide 1,2,3.R.A.Sheldon,J.K.Kochi "Metal-Catalysed Oxidation of Organic Compounds" Academic Press,New York (1981);F.Di Furia,G.Modena Rev.Chem.Interm. 6(1985)51; R.A.Sheldon Bull. Soc.Chim.Belg. 94(1985)651 and references therein.

Slide 4.R.E.Drew,F.W.B.Einstein Inorg.Chem. 11(1972) 1079; H.Mimoun,P.Chaumette,M.Mignard,L.Saussine,J.Fischer,R.Weiss Nouv. J. de Chemie 7(1983)467; S.E.Jacobson, R.Tang, F.Mares Inorg.Chem. 17(1978)3055; J.M.Le Carpentier,R.Schlupp,R.Weiss Acta Crystallogr.Sec. B 28(1972)1278.

Slide 5.J.M.Le Carpentier,R.Schlupp,R.Weiss Acta Crystallogr Sec. B 28(1972)1278; G.Amato, A.Arcoria, F.P.Ballistreri, G.A.Tomaselli,O.Bortolini,V.Conte,F.Di Furia,G.Modena,G.Valle J. Molec. Catal. in press.

Slide 6,7,.F.Di Furia,G.Modena Pure Appl.Chem. 54 (1982) 1853

Slide 8.D.Swern "Organic Peroxides" Wiley Interscience,Vol.2 (1971) 355; F.Di Furia,G.Modena,R.Curci,J.O Edwards Gazz.Chim.Ital. 109 (1979)571; R.Curci,F.Di Furia,G.Modena J.C.S. Perkin Tr.II (1977)576; H.Mimoun,I.Seree de Roch, L.Sajus Tetrahedron 26 (1970) 37.

Slide 9.R.Curci,J.O.Edwards "Organic Peroxides" Wiley, Vol.1 (1970)199;F.Di Furia,G.Modena unpublished results;F.Di Furia, R.Testi,G.Modena J.C.S.Perkin Tr.II (1974)752; R.Curci,F. Di Furia,G.Modena,J.C.S.Perkin Tr.II(1977)576; O.Bortolini, F.Di Furia,G.Modena,C.Scardellato,P.Scrimin J.Mol.Catal. 11 (1981) 107.

Slide 10.O.Bortolini,V.Conte,F.Di Furia,G.Modena unpublished results.

Slide 11.B.M.Trost,Y.Masuyama,Tetrah.Lett. 25 (1984) 173.

Slide 12.O.Bortolini,V.Conte,F.Di Furia,G.Modena J.Org.Chem. in press.

Slide 13.O.Bortolini,F.Di Furia,G.Modena to be published.

Slide 14. H.B.Henbest,R.A.L.Wilson J.Chem.Soc. (1957)1958; K.B.Sharpless,R.C.Michaelson J.Am.Chem.Soc. 95 (1973) 6136.

Slide 15 A. Arcoria,F.P.Ballistreri,G.A.Tomaselli,F.Di Furia, G.Modena J.Org.Chem. in press.

Slide 16.O.Bortolini,F.Di Furia,G.Modena J.Mol.Catal. 19 (1983) 319.

Slide 17.K.B.Sharpless,R.C.Michaelson J.Am.Chem.Soc. 95 (1973) 6136; K.B.Sharpless,T.R.Verhoeven Aldrichim.Acta 12 (1979)63; A.Arcoria, F.P.Ballistreri, G.A.Tomaselli, F.Di Furia,G.Modena J.Org.Chem. in press.

Slide 19.T.Katsuki,K.B.Sharpless J.Am.Chem.Soc. 102 (1980) 5974;M.G.Finn,K.B.Sharpless "Asymmetric Synthesis" (J.Morrison ed.)Vol.5 (1985)247.

Slide 20.I.D.Williams,S.F.Pedersen,K.B.Sharpless,S.J.Lippard J.Am.Chem.Soc. (1984) 6430; M.G.Finn,K.B.Sharpless "Asymmetric Synthesis" (J.Morrison ed.) Vol 5 (1985)247.

Slide 21.F.Di Furia,G.Modena,R.Seraglia Synthesis (1984)325; P.Pitchen,E.Dunach,M.N.Deshmukh,H.B.Kagan J.Am.Chem.Soc. 106 (1984)8188.

Slide 22.F.Di Furia,G.Modena,R.Seraglia Synthesis (1984) 325.

Slide 23.O.Bortolini,F.Di Furia,G.Modena,M.Rossi unpublished results.

Slide 24.R.Helder,J.C.Hummelen,R.W.Laane,J.S.Wiering,H.Wynberg Tetrah.Lett. (1976)1831; S.Colonna,H.Molinari,S.Banfi,S.Julia' J.Masana,A.Alvarez Tetrahedron 39 (1983)1635.

Slide 25.T.F.Levine .Biolog.Chem. 169 (1947)477; A. Maccioni, F.Montanari,M.Secci,M.Tramontin,Tetrah.Lett. (1961)607

Slide 26.O.De Lucchi,C.Marchioro,V.Lucchini,G.Valle,G.Modena J.C.S. Chem.Commun. (1985)878.

Slide 27.O.De Lucchi,M.Buso,G.Modena Tetrah.Lett. in press.

Slide 28.R.M.Dodson,N.Newman,H.M.Tsuchiya J.Org.Chem. 27 (1962) 2707; B.J.Auret,D.R.Boyd,H.B.Henbest,S.Ross J.Chem.Soc. C (1968)2371; S.W.May,R.S.Phillips J.Am.Chem.Soc. 1022 (1980) 5981.

Slide 29.S.W.May,R.D.Schwartz J.Am.Chem.Soc. 96(1974) 4031; H.Ohta,H.Tetsukawa J.C.S. Chem.Commun. (1978) 849.

AKNOWOLEDGEMENTS

I like to aknowoledge the fruitful collaboration with my colleques and students at Padova (Prof.F.Di Furia, Drs. O.Bortolini,V.Conte and Mrs. L.Bragante, S.Campestrini, A.Schionato) as well as the collaboration with the group at Catania (Profs. A.Arcoria and G.Tomaselli and Drs. F.P.Ballistreri ,G.Amato).