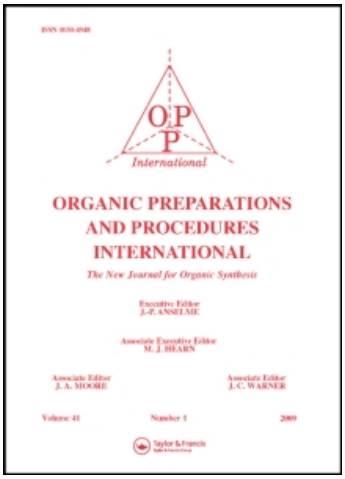

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INTRODUCTION

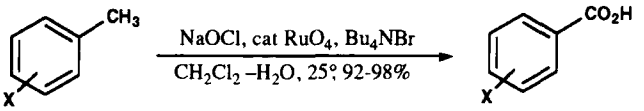
The ability of hypochlorites to oxidize various functional groups is well established in organic chemistry.[1] The synthetic use of these oxidants has been the subject of an exhaustive review published in Vol. 4/1a of Houben-Weyl's "Methoden der Organischen Chemie" covering literature up to 1980.[2] Since that time, its scope of application has expanded considerably because of the development of new catalytic systems. Thanks to these accomplishments, hypochlorites have today become one of the most versatile oxidants among single-oxygen donors.[3] In addition, hypochlorites are easily available, cheap, and enviromentally acceptable chemicals (bleaching agents).[4] For both reasons, they are ideally suited for application in laboratory syntheses as well as in scaled-up processes. Essentials of the inorganic chemistry of hypohalites (redox, pH-dependent equilibria, etc.) were briefly summarized by Downs and Adams.[5]

This article will focus on the new developments in the synthetic applications of hypochlorites which have not been covered in Houben-Weyl.[2] The subject matter is organized according to the types of compounds beingoxidized, as in Houben-Weyl. Besides the use of inorganic hypochlorites, new synthetic applications of *t*-butyl hypochlorite have also been reported.[103,104]

I. OXIDATION AT SATURATED CARBONS (sp^3)

1. Methyl Groups

Toluene and ring substituted methylbenzenes with electron-withdrawing substituents were oxidized with sodium hypochlorite to give the corresponding carboxylic acids in very high yields. The reaction was carried out in a two-phase system (CH_2Cl_2-water) in the presence of catalytic amounts of $RuCl_3 \cdot 3\,H_2O$ (1 mol%) and Bu_4NBr (5 mol%).[6]



X: H, *o*-NO_2, *m*-NO_2, *p*-NO_2, *o*-Cl, *p*-Cl, *o*-Br, *p*-Br, *p*-CN

This process is an example of the successful use of phase-transfer catalysis (PTC). Indeed, although the hypochlorite anion transferred into the organic phase as tetraalkylammonium salts is rather unstable, it often affords a high yield oxidation.[7]

2. Methylene Groups

Reactive methylene groups have occasionally been oxidized to the corresponding *gem*-diols, *e. g.* oxidation of the disodium salt of malonic acid gave the salt of the hydrate of ketomalonic acid[8] but in other cases this reaction led to decarbonylation.[8]

In the transformation of diolefins into isomerically pure diamines there is a step which parallels the corresponding methylene group oxidation. The intermediate boranes reacted with chloramines generated *in situ* to yield the desired diamines.[9]

$$R_2B\text{-}(CH_2)_n\text{-}Br_2 \xrightarrow[NaOCl,\ 0° \rightarrow \text{r.t.}]{R'NH_2,\ H_2O} R'NH\text{-}(CH_2)_n\text{-}NHR'$$

3. Hydroxymethyl Groups

a. Aldehyde Formation

Oxidation of primary alcohols to aldehydes requires carefully chosen reaction conditions to avoid overoxidation. Nevertheless, benzylic primary alcohols were converted easily to aldehydes with aqueous NaOCl under PTC conditions.[10-12]

TABLE 1. Oxidation of Benzylic Alcohols to Aldehydes[10]

Alcohol	Solvent	Time(min.)	Aldehyde(%)
$C_6H_5CH_2OH$	CH_2Cl_2	75	76
o-$MeOC_6H_4CH_2OH$	CH_2Cl_2	90	47
	AcOEt	72	94
p-$MeOC_6H_4CH_2OH$	CH_2Cl_2	75	79
	AcOEt	29	92
p-$MeC_6H_4CH_2OH$	CH_2Cl_2	83	78
	AcOEt	30	100
p-$ClC_6H_4CH_2OH$	CH_2Cl_2	60	82

Procedure.[10] *All oxidations were conducted with a 4-fold excess of 10% aqueous NaOCl, 0.4 M organic solution of the substrate and 5 mol% of tetrabutylammonium bisulfate. After control of the initial exotherm, stirring was continued at r.t. while the course of reaction was monitored by gas chromatography. Reaction times shown in the table indicate the time required to give the stated yield (This is the only reported procedure. No work-up was given)..*

For this reaction, an interesting and unexpected solvent specific effect was discovered with the use of ethyl acetate.[10,12] Alcohol oxidations were also carried out in a homogeneous reaction,[13,14] and

in a solid-liquid PTC system using an ion-exchanger.[15] However, when the two-phase reaction was carried out under certain conditions, benzyl benzoate was obtained along with benzaldehyde. The concentration of alcohol in the organic phase and the pH of the aqueous solution were crucial for the distribution of products: a dilute organic phase and low pH favored the formation of benzaldehyde. The ester was formed in a consecutive process promoted by a higher concentration of the organic phase.[16]

$$PhCH_2OH \xrightarrow[PTC]{[O]} PhCHO_{(org)} \xrightarrow{PhCH_2OH} PhCH(OH)OCH_2Ph \xrightarrow[PTC]{[O]} PhCO_2CH_2Ph$$

Sodium and calcium hypochlorites supported on basic alumina were also good oxidants for various benzylic alcohols,[17,18] whereas the reaction of primary and secondary alcohols was sluggish.[17]

Generally, the synthetic scope of oxidation expanded greatly through the use of catalysts transferring an oxygen from hypochlorite to the hydroxymethyl group. The first effective system of this kind was elegantly designed by Tabushi and Koga[19] using the *meso*-tetraphenylporphyrin-Mn(III) complex as a co-catalyst for the NaOCl/PTC oxidation of benzyl alcohol.[19] Moderate catalytic effects were observed in the oxidation of aliphatic alcohols with hypochlorites in the presence of ruthenium catalysts: ($RuO_2 \cdot 2H_2O$),[20,21] ($RuCl_3 \cdot xH_2O$).[21,22]

$RCH_2OH \longrightarrow RCHO$	
R: *n*-C_4H_9	49%[20]
n-C_9H_{19}	60%[21]
n-$C_{14}H_{29}$	45%[22]

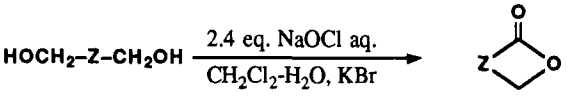
TABLE 2. Oxidation of Primary Alcohols to Aldehydes[23]

Alcohol	Aldehyde	Yield
1-pentanol	pentanal	99
1-heptanol	heptanal	98
1-nonanol	nonanal	98
1-undecanol	undecanal	98
$\overline{OC(CH_3)_2OCH_2CH(CH_2)_3CH_2OH}$	$\overline{OC(CH_3)_2OCH_2CH(CH_2)_3CHO}$	96
benzyl alcohol	benzaldehyde	95
m-nitrobenzyl alcohol	*m*-nitrobenzaldehyde	100
p-nitrobenzyl alcohol	*p*-nitrobenzaldehyde	100
p-methoxybenzyl alcohol	*p*-anisaldehyde	98

Procedure.[23] *A reaction flask thermostated at 0° was charged with 10.0 mL of a methylene chloride solution 0.4 M in the alcohol and 0.004 M in 4-MeO-TEMPO and 0.8 mL of a 0.5 M aqueous solution of KBr. At zero time, 14.3 mL of 0.35 M aqueous sodium hypochlorite at pH 8.6 (adjusted with solid sodium bicarbonate) was added and the mixture was stirred at 1300 rpm. At the end of the reaction, the organic phase was separated, dried over magnesium sulfate, evaporated, and purified by column chromatography on silica gel (only this general preparative procedure was reported).*

A major breakthrough in this transformation occurred with the catalytic application of oxammonium salts. Primary alcohols were quantitatively oxidized to aldehydes in a few minutes at 0° in CH_2Cl_2-0.35 M aqueous NaOCl in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-MeO-TEMPO). The addition of 0.10 mol equiv. of KBr and buffering of the solution at pH 8.6 with $NAHCO_3$ were also required.[23] The reaction can be considered the method of choice for preparation of aldehydes from simple primary alcohols.

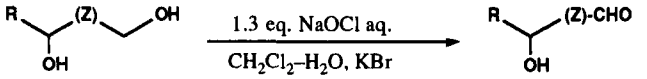
The same authors applied this successful procedure to the oxidation of diols.[24] They found that 1,10-undecanediol was converted into 10-hydroxyundecanal in 68% yield using 1.1 mol equiv. of oxidant; lactones were obtained in the oxidation of 1,4- and 1,5-diols.[24]



Z: $-(CH_2)_2-$ (69%)
$-(CH_2)_3-$ (58%)
$-CH_2N(Tos)CH_2-$ (85%)

Calcium hypochlorite has also been used occasionally as an alternative as the stoichiometric reagent for the two-phase oxidation of alcohols in the presence of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl; thus, 1-undecanal, 2-tetradecynal, and phenylacetaldehyde were obtained in 90, 96, and 82% yield, respectively.[25]

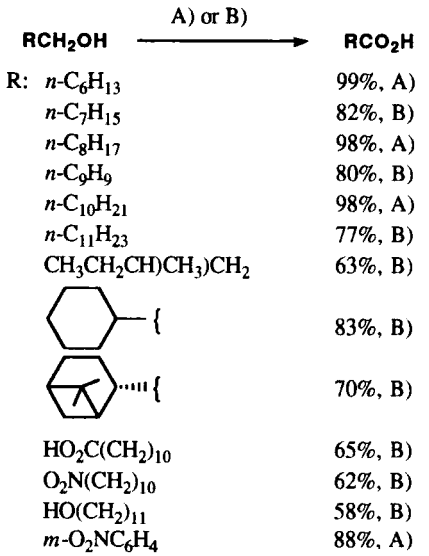
The selective oxidation of primary hydroxy groups in primary-secondary diols has been elaborated using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) instead of 4-MeO-TEMPO and, in contrast to the previous system,[23,24] by adding Bu_4NCl as a PTC catalyst.[26] The modified catalytic system oxidized various diols to the corresponding hydroxyaldehydes.[26]



R: Me,	Z: $-(CH_2)_2-$	43% as cyclic hemiacetal
Me,	$-(CH_8)_2-$	58%
Me,		65%
Me,	$>CH-C_6H_{13}-n$,	98%
$n-C_5H_{11}$,	$>CH-C_4H_9-n$,	76%
$C_{12}H_{25}$,	none	71% as dimer hemiacetal
$C_{12}H_{25}OCH_2$,	none	69% as dimer hemiacetal

b. Carboxylic Acid Formation

Primary alcohols were efficiently converted to the corresponding carboxylic acids by means of the above mentioned catalytic system: NaOCl-(4-MeO-TEMPO)-KBr with the use of PTC.[23] Also simple oxidation of alcohols using calcium hypochlorite in a CCl_4/*t*-BuOH mixture gave acids along with small amounts (5-10%) of esters.[27]



A) Aq. NaOCl (2.5 eq.), 4-MeO-TEMPO, KBr, Bu_4NBr, CH_2Cl_2-H_2O, 0°
B) Aq. $Ca(OCl)_2$, CCl_4-*t*-BuOH, r.t., 3, 5-7 hrs

c. Ester Formation

As already mentioned, oxidation of benzyl alcohol with NaOCl gave a mixture of benzaldehyde and benzyl benzoate.[16] Other primary alcohols were cleanly oxidized to esters using calcium and sodium hypochlorite, where both the acid and the alcohol parts of the ester were derived from the starting alcohol.[13]

TABLE 3. Oxidation of Primary Alcohols to Esters[13]

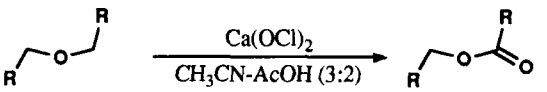
Alcohol	yield (%)	
	$Ca(OCl_2)$	NaOCl
1-pentanol	83	91
1-hexanol	98	98
3-methylbutanol	76	87
benzyl alcohol	—[a]	—[a]

a) In both cases, a 98% yield of benzaldehyde was obtained.

Procedure.[13] *The alcohol (19 mmol) dissolved in acetonitrile:acetic acid (3:2, 25 mL) was added*

dropwise over a period of 10 minutes to a cooled (0°) and stirred solution of calcium hypochlorite (1.48 g, 12.7 mmol) in water (40 mL). Stirring was continued for 1 hr after which water (40 mL) was added. The solution was extracted with methylene chloride (4 x 10 mL) and the organic layer was washed with 10% sodium bicarbonate and water. After drying over magnesium sulfate and evaporation, the crude product was distilled (This procedure was given for the oxidation of l-menthol to l-menthone. Oxidation of primary alcohols under indentical conditions gave esters).

Ethers were also converted to esters under these conditions.[13]



R: n-C_3H_7 40%
$-(CH_2)_2-$ 68%
$-(CH_2)_3-$ 56%

TABLE 4. Oxidation of Secondary Alcohols to Ketones

Alcohol	Product	Yield (%)[Ref.]
2-propanol	acetone	95[30]
2-pentanol	2-pentanone	87[13]
3-pentanol	3-pentanone	91,[13] 97[13]
2-octanol	2-octanone	99,[23] 80,[13] 99,[13] 96[14]
2-nonanol	2-nonanone	98[23]
cyclopentanol	cyclopentanone	89[10]
cyclohexanol	cyclohexanone	98,[23] 98,[13] 96,[14] 80[30]
cycloheptanol	cycloheptanone	92[30]
2,6-$(Me)_2$-cyclohexanol	2,6-$(Me)_2$-cyclohexanone	60[30]
3,5-$(Me)_2$-cyclohexanol	3,5-$(Me)_2$-cyclohexanone	93[13]
4-*t*-butylcyclohexanol	4-*t*-butylcyclohexanone	49[10]
2,2,5-$(Me)_3$-cyclohexanol	2,2,5-$(Me)_3$-cyclohexanone	90[14]
2-($TosCH_2$)-cyclohexanol	2-($TosCH_2$)-cyclohexanone	98[13]
menthol	menthone	98,[13] 92,[28] 94[14]
borneol	camphor	98,[13] 99,[13] 95[14]
norborneol	norcamphor	92,[13] 92[14]
9-cyanoisoborneol	9-cyanocamphor	94[14]
diphenylcarbinol	acetophenone	98[13]
1-Ph-2-($TosCH_2$)-ethanol	α-($TosCH_2$)-acetophenone	98[13]
5-Cholesten-3-ol	4-Cholesten-3-one	91,[13] 91[13]
5α-Androstane-3β,17β-diol	5α-Androstane-3,17-dione	96[14]
2-ethyl-1,3-hexanediol	2-ethyl-1-hydroxy-3-hexanone	85[14]

Oxidation of Cyclohexanol.[14] *Cyclohexanol (99.0 g, 0.988 mol) was dissolved in glacial acetic acid (660 mL) in a 2L 3-neck flask fitted with a mechanical stirrer and a thermometer. Aqueous sodium hypochlorite (660 mL of 1.80 M soln, 1.19 mol) was added dropwise over 1 hr. The reaction was cooled in an ice-bath to maintain the temperature in the 15-20° range. The mixture was stirred for 1 hr after the addition was complete and saturated aqueous sodium bisulfite solution (3 mL) was added until the starch iodide test was negative (color changed from yellow to colorless). The mixture was then poured into ice-brine (2 L) and the product was extracted six times with ether. The organic layer was washed with aqueous sodium hydroxide (5% by weight) until the aqueous layer was basic (pH test paper). The aqueous washes were then combined and extracted five times with ether. The ethereal layers were combined and dried over magnesium sulfate. The ether was distilled through a 30-in. Vigreux column until less than 300 mL of solution remined. The remainder was fractionally distilled through a 12-in. Vigreux column. After a forerun of ether, cyclohexanone (bp. 155°) was distilled to give 92.9 g (96%) of a colorless liquid which had ^1H NMR and IR spectra and GC retention time identical with those of an authentic sample. (For other procedures, see also footnotes to Table 1 and Table 3.)*

The catalytic oxidation of benzylalkyl, dialkyl, and cyclic ethers with $RuCl_3$/NaOCl or $Ca(OCl)_2$ in CH_2Cl_2-H_2O at room temperature and under PTC conditions also produced the corresponding esters in up to 65% yield.[28]

4. Hydroxymethylene Groups

Aqueous sodium hypochlorite and solid calcium hypochlorite are extremely effective and superior to more exotic reagents for the oxidation of secondary alcohols to ketones. These reactions do not require an oxygen-transfer catalyst. They were successfully performed in homogeneous systems of acetic acid[14] and an acetic acid-acetonitrile mixture[13] in micellar media[29] as well as in biphasic system of methylene dichloride-water/PTC,[10] the triphasic system (solid $Ca(OCl)_2$-IRA 900 resin-CCl_4)[30] and, for benzylic alcohols only, with hypochlorites supported on alumina[18] and silica gel.[31] Primary alcohols react sluggishly under all these conditions and the direct non-catalyzed oxidation can be recommended specifically for the transformation of secondary alcohols into ketones. Competitive reaction between cycloheptanol and *n*-heptanol resulted in the oxidation of the secondary alcohol (85%) with excellent recovery (98%) of the primary alcohol.[14] The oxidation of 2-ethyl-1,3-hexanediol to 2-ethyl-1-hydroxy-3-hexanone (85%)[14] demonstrates this remarkable selectivity. Additionally, it was documented in a systematic study that a variety of diols were oxidized with aqueous solutions of NaOCl in acetic acid to afford the corresponding hydroxy ketones in good yields.[32]

1,2-Diphenyl-1,2-ethanediol afforded benzoin (85%) or benzil (97%) in the oxammonium salt mediated oxidation with 1.1 or 2.2 equiv. of aqueous NaOCl, respectively.[24]

The reaction of benzhydryl halides with aq. NaOCl in acetonitrile in the presence of Bu_4NHSO_4 gave the corresponding ketones.[33] Similar treatment of secondary benzylic bromides using ultrasonic irradiation instead of PTC also gave the respective ketones.[34] This reaction was shown to proceed *via* the corresponding alcohols.[34]

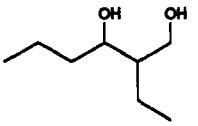
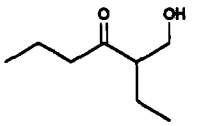
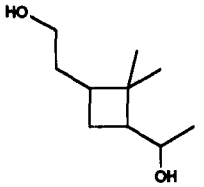
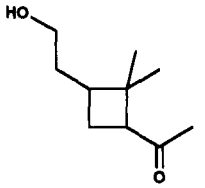
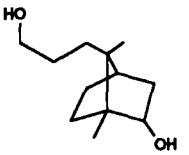
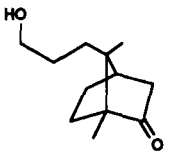
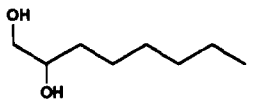
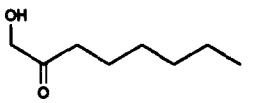
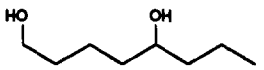
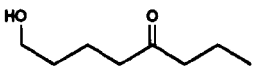
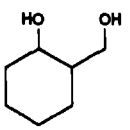
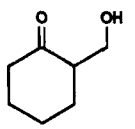
II. OXIDATION AT UNSATURATED CARBONS (sp^2)

1. Olefin Epoxidations

a. Catalytic Systems

The catalytic oxidation of olefins has been an area of intensive research for the last decade and hypochlorites have been effectively applied in this field as a convenient oxygen source when activated by the presence of various transition-metal complexes.[35] The efficiency of catalytic oxidant depends upon several features: i) the type of catalyst-complex used (both, metal and ligand), ii) the presence of an additional axial ligand, iii) the state of equilibria in the aqueous phase (pH, PTC) and iv) the structure of olefin being oxidized.

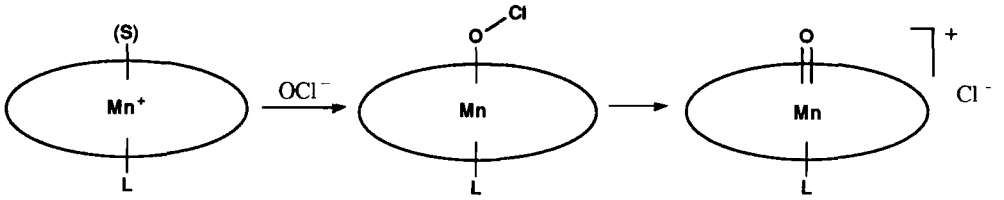
TABLE 5. Selective Oxidation of Diols to Hydroxy Ketones

Diol	Product	Yield (%)
		85
		83
		91
		73
		70
		90

Procedure.[32] *The diol (3.71 mmol) was dissolved in 3 mL of glacial acetic acid and stirred magnetically. The dropwise addition of an aqueous 1.86 M NaOCl (2.1 mL, 1.05 equiv) at r.t. over 15 min initiated a rapid exothermic reaction. Stirring was continued for 1 hr at r.t., after which 2 mL of isopropanol was added to quench any remaining oxidant followed by 50 mL of water. The solution was extracted 3 times with methylene chloride, washed with aqueous sodium bicarbonate and dried over magnesium sulfate. Removal of the solvent left crude material, which could be purified by column chromatography on florisil.*

The major part of work has been done with manganese porphyrines;[36-73] however, other Mn, Fe, Co, and Ni complexes have also been tested successfully.[45,74-83] The Meunier system (NaOCl/Mn(III) porphyrin complex)[45] is the best oxidant of metalloporphyrines type.[45,69] However, when the transition-metal phthalocyanines are considered, the Co(II) and Ni(II) derivatives are better catalysts than Mn and Fe.[74] More recently, the nickel complexes of salen- and cyclam-type ligands[75-78] as well as the simple complexes of 2,2'-bipyridine, and 1,10-phenanthroline[79] have been reported as effective catalysts in epoxidation with NaOCl. The chiral, salen-type complexes of manganese have become highly valuable catalysts in the enantioselective epoxidation of unfunctionalized olefins.[80-83]

The overall epoxidation process with the Meunier system consists of a binding of hypochlorite anion to the catalyst followed by the rearrangement of the new complex into an electrophilic oxo-species, which, in turn, transfers an oxygen atom to the olefin molecule. In spite of the disputed kinetics of the catalytic cycle (*e. g.*, see: ref. 59), it is generally accepted that a facile formation of the activated metal-oxo complex with the positive charge stabilized by the proper coordination environment is crucial for effective catalysis.



In the case of active catalysts, performance depends primarily on the stability of the complex towards oxidative destruction. Many studies have demonstrated that both steric and electronic effects play an important role in the stabilization of catalyst. For this reason, in the epoxidation of less reactive, terminal olefins, where longer reaction times are required, only the most robust manganese porphyrines, *e. g.* the tetra(2',6'-dichlorophenyl) analogue,[64] can be effectively used. Generally, manganese *meso*-tetraphenylporphyrines bearing large and/or electron-withdrawing substituents in the *ortho*-positions of the phenyl rings are protected against oxidative degradation. Moreover, the presence of steric hindrance around the metal center is a key factor for the stereoselectivity of epoxidation. Also the use of polymer bound manganese porphyrines produces more oxidation resistant catalysts and increases the rate of epoxidation.[52, 54, 73]

Additional axial ligands, such as pyridines and N-substituted imidazoles, enhance the reaction rate and yield and also increase the stereoselectivity of epoxidation. These ligands stabilize the oxo-species by preventing the formation of μ-oxo dimers. It was found that the beneficial influence of the ligand correlated with its σ-donating properties, *e. g.* 4-MeC_5H_4N > C_5H_5N > 4-$(CN)C_5H_4N$.[37] The ligand must be used in stoichiometric excess over the Mn-porphyrin catalyst since it is oxidized along with the epoxidation and for this reason the oxidation of poorly reactive substrates such as terminal olefins required high [ligand]/ [Mn-porphyrin] values.[65]

The phase-transfer agent plays an essential role for the two-phase epoxidation with the Meunier system at the pH of commercial bleach.[62,65] The epoxidation rate increases with decreasing pH of the aqueous solution[58,62,65] and the rate is then only slightly affected by PTC.[62,65] This effect is explained by a fast formation of the oxo-species due to the presence of hypochloric acid.[58,65] On buffering the pH at 10.5 both the epoxide selectivity and the reaction rate remain satisfactorily high, while at 9.5 the chlorination reaction becomes important, lowering markedly the epoxide selectivity.[65]

The order of olefin reactivity observed in the catalytic epoxidation with the Meunier system is different from that in electrophilic epoxidation with peracids, namely: styrene > *cis*-2-hexene > tetramethylethylene > 1-methylcyclohexene > cyclohexene > 2-methyl-1-heptene > *trans*-2-hexene (determined from independent reactions).[50] It is noteworthy that, unlike the latter oxidant, the catalytic epoxidation of *cis*-olefin is much faster than that of the *trans*-isomer. Competition experiments show that a less hindered substrate ties up the active catalyst thus preventing the oxidation of the even more nucleophilic but bulky olefin.[47] Also the non-conjugated dienes of varying shapes show enhanced selectivity for epoxidation of the most exposed double bond of the substrate.[48,72]

b. Epoxide Formation

Although most investigators report kinetic experiments, a few preparative epoxidations have been described. The Meunier system was highly efficient for the epoxidation of styrene, tetra-, tri-, and disubstituted olefins, while terminal olefins, as already mentioned, required the modified porphyrin catalysts.[42]

Electron-defficient alkenes were epoxidized smoothly when 2 M aq NaOCl was added to the alumina- or montmorillonite-supported alkene.[84] Also silica gel-supported 3-hydroxy-1-alkenes were oxidized under these conditions initially to the ketones followed by epoxidation to acyloxiranes.[31]

c. Stereo- and Enantioselectivity of Epoxidation

Aliphatic olefins are epoxidized with the Meunier system stereospecifically (*syn*-addition of the oxygen atom); thus *cis*-2-hexene gives only the *cis*-epoxide, *trans*-2-hexene affords the *trans*-isomer; the reaction of norbornene leads to the exo-epoxide; 3-carene forms α-3,4-epoxycarane and α-pinene gives α-pinene oxide, all reactions occur with the same stereochemistry as that observed using peracid.[40,45] However, with non-aliphatic olefins this stereospecifity is less pronounced and the results depend upon the presence of axial ligand,[45] or the use of sterically hindered metalloporphyrin.[44,48] On the other hand, the epoxidation of *cis*-olefin catalyzed by Ni-phthalocyanin gave a 0.17

ratio of *cis/trans* epoxides.[74]

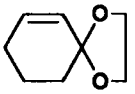
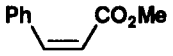
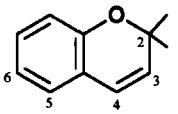
The enantioselective epoxidation of unfunctionalized olefins is a challenging synthetic problem. The Meunier system with the chiral α,β,α,β-atropoisomer of tetrakis[(R)-1,1'-binaphth-2-yl]porphyrin as a catalyst gave high catalytic efficiency but only moderate enantioselectivity of epoxidation for styrene, *p*-chlorostyrene, 2-vinylnaphthalene (20% ee's), (E)-β-methylstyrene (15% ee), and (Z)-β-methylstyrene (40% ee).[60] Recently, Jacobsen and collaborators have developed a new practical method for this important transformation.[80-83] They used chiral Mn(III)Salen complexes and obtained, in the epoxidation with aqueous NaOCl, up to 98% ee and 51-96% isolated yields. The optimal

TABLE 6. Catalytic Oxidation of Olefins to Epoxides

Olefin	Catalyst	Yield of Epoxide (%)[Ref.]
styrene	Mn^{III}Porph	36,[36] 80,[37] 90,[44] 80[73]
	Co^{II}PC	58[74]
	Ni^{II}Salen	44[75]
	Ni^{II}Bpy	74[79]
2-methyl-2-heptene	Mn^{II}Porph	60[45]
1-methylcyclohexene	Mn^{III}Porph	92,[44] 70[45]
3-carene	Mn^{III}Porph	60[40]
α-pinene	Mn^{III}Porph	52[40]
(Z)-β-methylstyrene	Ni^{II}Salen	44[75]
	Fe^{III}Porph	68[76]
	Co^{II}PC	30[74]
(E)-β-methylstyrene	Ni^{II}Salen	89,[75] 51[78]
norbornene	Ni^{II}Salen	30[75]
	Mn^{III}Porph	98[44]
cyclohexene	Ni^{II}Salen	23[75]
	Mn^{III}Porph	97,[44] 72[45]
cyclooctene	Mn^{III}Porph	86,[45] 96,[62] >85[64]
(Z)-stilbene	Co^{II}PC	88[74]
2-methyl-1-heptene	Mn^{III}Porph	42[45]
α-methylstyrene	Mn^{III}Porph	95[45]
	Ni^{II}Bpy	53[79]
vinylcyclohexane	Mn^{III}Porph	50[42]
propene	Mn^{III}Porph	51[42]
1-octene	Mn^{III}Porph	81,[42] 68[44]
1-dodecene	Mn^{III}Porph	90[64]
5-bromo-1-pentene	Mn^{III}Porph	69[42]
4-penten-1-yl acetate	Mn^{III}Porph	41[42]

Procedure.[40] *A solution of the olefin (4 mmol) in 10 mL of methylene chloride containing Mn(tetraphenylporphyrine) (OAc) (0.04 mmol), dimethylbenzyldodecylammonium chloride (0.05 mmol) and pyridine (0.62 mmol) was stirred with 20 min. of 0.35 mL NaOCl under nitrogen at r.t. (no further experimental details were provided).*

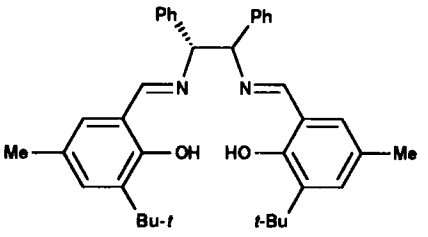
TABLE 7. Asymmetric Epoxidation of Olefins

Olefin	Catalyst	[Enantiomeric Excess,(%)] Yield of Epoxide, (%)[Ref.]
(Z)-β-methylstyrene	$Mn^{III}Salen^1$	[86], 80[80]
	$Mn^{III}Salen^2$	[92], 84[81]
(Z)-*p*-chloro-β-methylstyrene	$Mn^{III}Salen^2$	[92], 67[81]
	$Mn^{III}Salen^2$	[94], 63[81]
	$Mn^{III}Salen^2$	[89], 65[81]
	$Mn^{III}Salen^2$	[98], 72[81]
R^3, R^4, R^5, R^6: H	$Mn^{III}Salen^2$	[98], 87[83]
R^3, R^4, R^5: H, R^6: CN	$Mn^{III}Salen^2$	[97], 96[81]
	$Mn^{III}Salen^2$	[97], 96[83]
R^3, R^4, R^5: H, R^6: NO_2	$Mn^{III}Salen^2$	[94], 76[83]
R^3, R^5, R^6: H, R^4: CH_3	$Mn^{III}Salen^2$	[97], 51[83]
R^4, R^5: H, R^3:CH_3, R^6: CN	$Mn^{III}Salen^2$	[>98], 82[83]
R^3, R^4: H, R^5: OMe, R^6: Ac	$Mn^{III}Salen^2$	[98], 75[83]

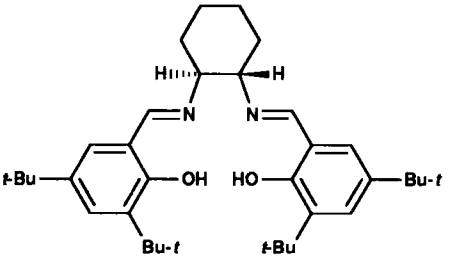
Procedure.[81] *A solution of commercial household bleach was diluted with 0.05 M disodium phosphate to approximately 0.55 M in NaOCl and the pH of the resulting buffered solution was adjusted to pH = 11.3 by addition of a 1M NaOH solution. To this solution was added a solution of Mn(Salen²)(Cl) (159 mg, 0.25 mmol) and the olefin (12.5 mmol) in 12.5 mL of methylene chloride. The two-phase mixture was stirred at 4°, and the reaction progress was monitored by TLC. After 6 hrs, 12.5 mL of methylene chloride was added to the mixture and the organic phase was separated, washed twice with 50 mL of water and once with 50 mL of brine, and then dried over sodium sulfate. After the solvent removal, the residue was purified by flash chromatography on silica gel.*

catalyst ($Salen^2$) was prepared in two simple steps from the readily available chiral 1,2-diaminocyclohexane.[81] This method is currently the most effective asymmetric catalytic epoxidation developed for simple olefins and provides a practical access to optically pure epoxides. Reactions carried out with

the opposite enantiomer of catalyst gave products of opposite configuration. Better face selectivity in the case of complexation with Salen[2] is attributed to the larger *t*-butyl groups limiting approaches of substrate other than that from the side of cyclohexane moiety. In such a reaction mode, the bulkier substituent on the substrate is directed away from the axial hydrogen on the bridge. This is in full agreement with the low reactivity and selectivity observed for *trans*-olefins as well as with the lower selectivity (60-75% ee) obtained for terminal olefins such as styrene.[81]



Salen[1]

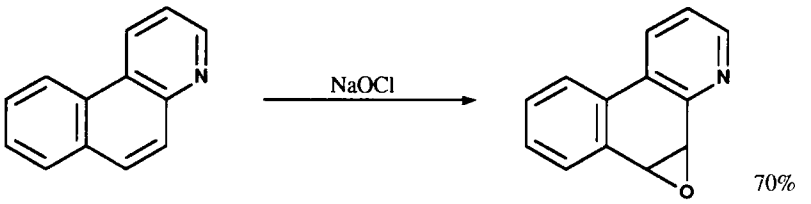


Salen[2]

2. Oxidation of Aromatic Systems

a. Epoxide Formation

Azaphenanthrenes were successfully epoxidized with aqueous hypochlorite under the PTC conditions and at the pH adjusted to 8-9.[85]



70%

b. Quinone Formation

Various alkyl- and aryl-substituted catechols and hydroquinones were oxidized with sodium hypochlorite to give the corresponding *o*- and *p*-benzoquinones in high yields. The reactions were carried out in in a two-phase system ($CHCl_3$-H_2O) in the presence of a tetrabutylammonium salt at 25° (hydroquinones) or -10 to -5° (catechols).[11]

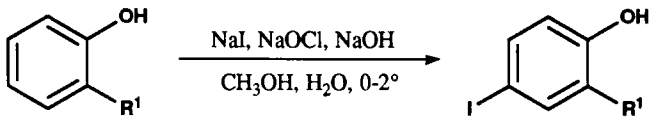
c. Oxidative Halogenation

Although radical substitution is beyond the scope of this review, it is worth noting that PTC markedly increases the regioselectivity of ring monochlorination with aqueous NaOCl.[86]

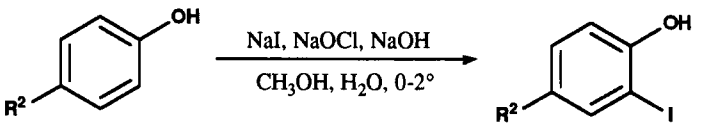
An efficient and selective method for the preparation of iodophenols was developed using the NaOCl-promoted iodination of *o*- and *p*-substituted phenols; 3-hydroxypyridine was converted into 2-iodo-5-hydroxypyridine (75%).[87]

Sodium hypochlorite induced the oxidative exchange of bromine for chlorine in aromatic

compounds. These ipso substitutions were catalyzed either by the nickel complexes[88] or photochemically.[89]



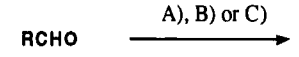
R^1: H, CH_3, Ph, Cl, I — 74-84%



R^2: Ph, COOH, NO_2, Cl — 66-86%

3. Oxidation at Carbonyl Carbon Atom

Calcium hypochlorite in aqueous acetic acid-acetonitrile solution at room temperature was an efficient oxidant for conversion of aldehydes into carboxylic acids.[90] Aliphatic aldehydes and aromatic aldehydes with electron-withdrawing substituents gave the acids in high yields, while nuclear chlorination occurred preferentially with aromatic aldehydes bearing electron-donating groups.[90] Aromatic aldehydes were also converted into acids using aqueous sodium hypochlorite in a liquid-liquid PTC system with tetrabutylammonium bromide as a catalyst.[91] In the case of anisaldehyde,[91] alkaline PTC oxidation gave *p*-methoxybenzoic acid (92%), whereas the reaction in the presence of acetic acid led to 3-chloro-4-methoxybenzoic acid (76%). Although oxidation of aldehydes to acids by NaOCl in the



R:		
n-C_6H_{13}	70%, A);	96%, C)
n-C_8H_{17}		98%, C)
n-$C_{10}H_{21}$		98%, C)
$(C_2H_5)_2CH$	75%, A)	
cyclo-C_6H_{11}	77%, A)	
C_6H_5	86%, A);	87%, B)
p-$(CH_3)_2CHC_6H_4$		84%, B)
p-$MeOC_6H_4$		92%, B)
m-$O_2NC_6H_4$	84%, A)	87% C)
o-$O_2NC_6H_4$		71%, B)
o-ClC_6H_4	81%, A)	
p-ClC_6H_4	92%, A);	88%, B)
p-BrC_6H_4		82%, B)

A) Aq. $Ca(OCl)_2$, CH_3COOH-CH_3CN, r.t., 16 hrs[91]

B) Aq. NaOCl, Bu_4NBr, CH_2ClCH_2Cl-H_2O, r.t., 3 hrs[92]

C) Aq. NaOCl, $-MeO-TEMPO, KBr, Aliquat 336, CH_2Cl_2-H_2O, 0° , 5 min[23]

two-phase 4-MeO-TEMPO mediated reaction was slow, aliphatic aldehydes and *m*-nitrobenzaldehyde were oxidized smoothly to the corresponding acids by addition of Aliquat 336 as a phase transfer catalyst.[23] In strongly alkaline NaOCl solution, furfural and 5-methylfurfural formed acids in 58 and 65% yield, respectively.[93]

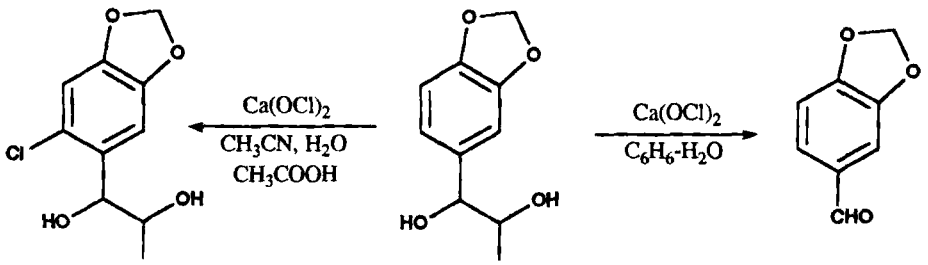
III. OXIDATION INVOLVING CLEAVAGE OF CARBON-CARBON BONDS

1. Oxidative Cleavage of Double Bonds

A catalytic procedure for the preparation of glutaric acid by an oxidative cleavage of cyclopentene has been patented.[93] The olefin was oxidized with strongly alkaline aq NaOCl in the presence of ruthenium catalyst to give the product in 71-79% yield.[93]

2. Oxidative Cleavage of *vic*-Diols

vic-Glycols were easily cleaved with $Ca(OCl)_2$.[94] Pinacol, benzopinacol, cyclohexanone-pinacol (with 2 equiv. of hypochlorite) and of 2,3-butanediol and 1,2-diphenyl-1,2-ethanediol (with one equiv. of hypochlorite) were oxidized to the corresponding ketones and aldehydes in good to excellent yields; on the other hand, propylene and 1-phenylethylene glycols were cleaved directly to acetic and benzoic acids, respectively.[94] The reactions were carried out in aqueous acetonitrile and acetic acid at room temperature for 1-4 hrs.[94] Under these conditions, isosafrole glycol underwent chlorination on the aromatic ring only,[95] however, in the two-layer system of C_6H_6-H_2O with 2 equiv. of Ca(OCl) at 65°, the desired cleavage to piperonal was achieved quantitatively.[95]



A new convenient method for the practical preparation of protected optically pure D- and L-glyceric acid was developed using, as a key step, the ruthenium catalyzed hypochlorite cleavage of protected diols and α-hydroxy acids.[96] The oxidation was conducted in water in the presence of various ruthenium catalysts, both homogeneous and heterogeneous, and the pH was maintained at 8 by addition of a NaOH solution. These conditions resulted in an efficient and non-racemized cleavage of 1,2:5,6-di-O-isopropylidene- and 1,2:5,6-di-O-cyclohexylidene-D-mannitol to the corresponding derivatives of D-glyceric acid.[96]

3. Oxidative Cleavage of α-Substituted Carbonyl Compounds

a. Oxidative Decarboxylations

Under slightly acidic conditions, α-hydroxy and α-keto aliphatic acids were cleaved with

$Ca(OCl)_2$ to smaller carboxylic acid derivatives.[94]

$$\text{RCH(OH)CO}_2\text{H or RCOCO}_2\text{H} \xrightarrow[\text{CH}_3\text{CN, H}_2\text{O, CH}_3\text{COOH, r.t.}]{\text{Ca(OCl)}_2} \text{RCO}_2\text{H}$$

a. R = $CH_3CH(CH_3)CH_2$- a. 70%
b. R = n-C_3H_7- b. 92%
c. R = $CH_3CH(CH_3)CH_2$- c. 96%

The ruthenium catalyzed NaOCl oxidation of 3,4-O-isopropylidene- and 3,4-O-cyclohexylidene-D-erythronic acid and their epimers (protected L-threonic acid) correspondingly gave the protected, optically pure, D- and L-glyceric acid in 93-99% yields.[96]

In the case of α-hydroxyphenylacetic acid, the oxidation with $Ca(OCl)_2$ in the presence of acetic acid gave benzaldehyde (84%).[94] When acetic acid was omitted, the hypochlorite oxidation of α-hydroxycarboxylic acids generally led to aldehydes or ketones as the only products and in good yields.[97]

$$\text{RCH(OH)CO}_2\text{H} \xrightarrow[\text{Et}_2\text{O, H}_2\text{O, 0°, r.t.}]{\text{NaOCl}} \text{RCHO}$$

TABLE 8. Oxidation of α-Hydroxy Carboxylic Acids[97]

Substrate	Product	Yield (%)
PhCH(OH)COOH	PhCHO	95
$Ph_2C(OH)COOH$	Ph_2CO	91
$PhC(CH_3)(OH)COOH$	$PHCOCH_3$	93
$C_6H_{11}CH(OH)COOH$	$C_6H_{11}CHO$	85
$(CH_3)_2CHCH(OH)COOH$	$(CH_3)_2CHCHO$	47
PhCH(OH)COONa	PhCHO	93
5-Androsten-3β,17α-diol-17-carboxylic acid	5-Androsten-3β-ol-17-one	85

Procedure.[97] *A solution of the α-hydroxycarboxylic acid in 25 mL of diethyl ether was cooled in an ice-bath. Then 40 mL of commercial bleach solution (4.2% NaOCl, 0.5% NaOH) (22 mmol) was added over a 3 min period. The reaction mixture was then allowed to warm up to r.t. and stirred at this temperature for 2-3 hrs. The organic layer was separated, washed with water, dried over magnesium sulfate and the solvent evaporated. The crude product was purified by molecular distillation or recrystallization (only this general procedure was included).*

Benzophenone was obtained in the hypochlorite oxidations of α-hydroxydiphenylacetic acid (69%)[98] and triphenylacetic acid (80-84%).[99]

b. Oxidative Cleavage of α-Hydroxy Ketones and α-Diones

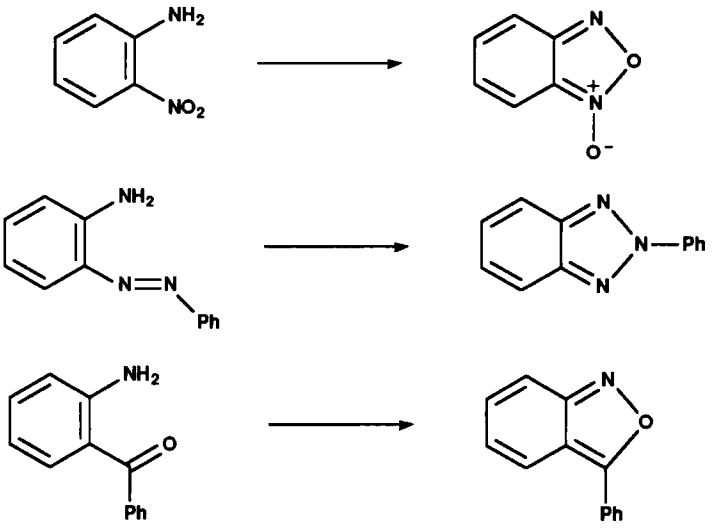
Benzoin, α-hydroxyacetophenone, and α-hydroxycyclohexanone as well as benzil and biacetyl were cleaved oxidatively to the corresponding acids (benzoic, acetic, and adipic) in the reac-

tion with $Ca(OCl)_2$ in a slightly acidified medium.[94]

IV. OXIDATION AT HETEROATOMS

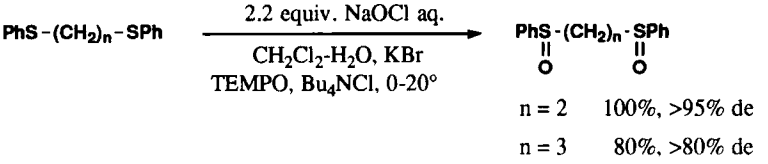
1. Oxidation at Nitrogen

2-Substituted anilines were N-chlorinated with alkaline sodium hypochlorite and eventually gave azaheterocycles.[100] The cyclization step was postulated to occur by internal capture of the putative nitrene by the *ortho* substituent.



2. Oxidation at Sulfur

Thioethers were effectively oxidized to the corresponding sulfoxides using the two-phase NaOCl/PTC[101] and NaOCl/alumina[18] procedures. Morever, 1,2- and 1,3-di(phenylthio)substituted derivatives underwent catalytic oxidation (NaOCl/TEMPO/PTC, CH_2Cl_2-H_2O)[26] to monosulfoxides (1.2 equiv. of hypochlorite), or diastereoselectively, to *meso*-disulfoxides.[102]



V. CONCLUSIONS

In conclusion, the new procedures constitute very mild and efficient methods for the selective oxidation of various functional groups. Particularly, the enantioselective epoxidation of unfunctionalized olefins and the selective oxidations of primary and secondary alcohols are recommended as the methods of choice for these transformations. Further useful applications of hypochlorites can be predicted as a result of the future development of new catalytic systems.

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