CHAPTER 3

THE BAEYER–VILLIGER OXIDATION OF KETONES AND ALDEHYDES

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INTRODUCTION

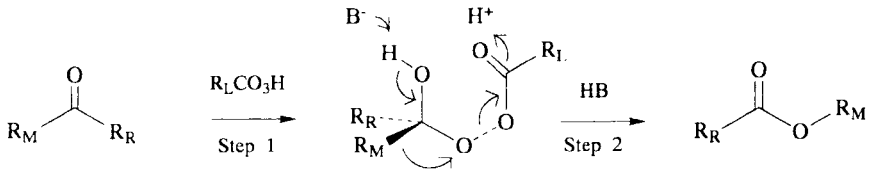
The oxidative conversion of alicyclic ketones into lactones with permonosulfuric acid was discovered by Baeyer and Villiger in 1899,[1] and in their honor the general process by which ketones are converted into esters or lactones is now known as the Baeyer–Villiger reaction. The literature on this synthetically useful process has been reviewed comprehensively through 1953 in Volume 9 of *Organic Reactions*,[2] and less comprehensive reviews of the reaction have appeared since then.[3-10g] More recent investigations have led to the development of new synthetic reagents, to improvements in experimental reaction conditions, and to a better understanding of regiochemical and stereochemical aspects of the reaction. Baeyer–Villiger reactions now often can be carried out with functional group chemoselectivity and regiochemical control. Although the recent removal from commerce of 90% hydrogen peroxide and reagents based upon this oxidant are a setback to Baeyer–Villiger reaction methodology, alternative reagents, catalysts, and methods described in this review are available to fill the gaps.

The definition of the Baeyer–Villiger reaction is somewhat fuzzy, and can be considered to include both ketones and aldehydes. In addition to the traditional use of organic and inorganic peracids as oxidants, examples of oxygen insertion reactions using hydrogen peroxide, alkyl peroxides, and several metal ion oxidants are considered to fall within the scope of this chapter and are included in the tabular survey.

MECHANISM

The Criegee Mechanism

The two-step ionic mechanism for the Baeyer–Villiger oxidation outlined by Criegee[11] continues to be generally accepted. Evidence for this mechanism obtained prior to 1953 is discussed in the previous review of this reaction.[2] As shown in Eq. 1, addition of peracid in step 1 to the ketone carbonyl provides a tetrahedral intermediate **1**. This step can be catalyzed by acid or base.[12] In step 2 the group R_M migrates with retention of configuration to oxygen as the O–O bond breaks and releases the leaving group to provide product ester or lactone.



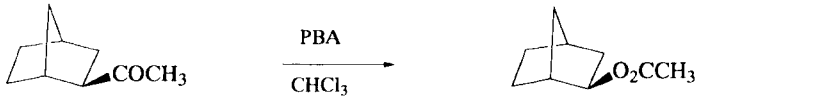
1

The two-step ionic mechanism for the Baeyer-Villiger reaction.

(Eq. 1)

Nature of the Migration Step

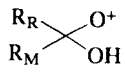
Evidence in support of a concerted migration step 2 includes stereochemical and isotopic labeling results, kinetic studies, and theoretical calculations. The migrating group is not free, since oxidation of (n)-*exo*-norbornyl ketone **2** with perbenzoic acid (PBA) in chloroform provides *exo*-acetate **3** with 94–100% retention of optical purity. Failure to observe racemization or *exo/endo* isomerization indicates the migrating group moves with its electrons.[13]



(–) (–) 94-100% retention (86%)

2 **3**

The leaving group does not leave intermediate 1 prior to migration. Oxidation of ^{18}O-carbonyl labeled benzophenone, *p*-methoxybenzophenone, and fluorenone with 40% peracetic acid/acetic acid/chloroform provides ester with the isotopic label in the carbonyl oxygen. This excludes a mechanism with equivalent oxygens such as an intermediate oxonium ion species **4** in which hydrogen exchange might occur.[14] Also, in the oxidation of cyclohexyl phenyl ketone in ethylene chloride at 30° there is a greater regioselectivity for cyclohexyl migration with peracetic acid than trifluoroperacetic acid (TFPAA). This result is inconsistent with a common intermediate, such as an oxonium ion, and suggests that migration occurs while the carboxylic acid residue is leaving the Criegee intermediate.[15]



4

Isotope effects support a migration in concert with departure of the leaving group. A secondary beta deuterium–isotope effect $k_H/k_D = 1.052/D$ is calculated for the TFPAA oxidation of phenyl-2-propanone. The positive value indicates a partial carbonyl bond adjacent to the nonmigrating methyl group in the transition state **5** for shifting of the benzyl group.[16] Significant ^{14}C isotope effects when X = CN, Cl, H, CH_3 (k_{12}/k_{14} = 1.084 to 1.032) are found for *m*-chloroperbenzoic acid

5

(MCPBA) oxidation of *para*-X-substituted acetophenones-1-^{14}C. The isotope effects are expected for rate-determining aryl migration from **1** in step 2, but rule out both formation of the Criegee intermediate and breaking of the O–O bond without concomitant rearrangement as rate-determining steps.[17]

Theoretical models, which trace the timing of the migration from carbon to oxygen during step 2 of the Baeyer–Villiger rearrangement, are consistent with the experimental results. MINDO-3 calculations rule out rate-determining migration to a cationic oxygen for reaction of performic acid with cyclobutanone.[18] Nonempirical SCF-MO and CNDO/2 treatments, which trace methyl migration in a model reaction, indicate little reorganization in the migrating methyl group and considerable carbonyl formation.[19]

Rate-Determining Migration

Most evidence indicates that the concerted migration step 2 is rate determining.[16,17,20,21] Aryl substituents do not affect the Baeyer–Villiger reaction of aryl ketones in the same way as reactions known to proceed by rate-determining addition. For example, rates of simple carbonyl addition reactions such as oximation and semicarbazone formation can be correlated by a linear free energy relationship,[22] but a linear relationship does not exist between the free energies of activation for the Baeyer–Villiger reaction of dialkyl, cycloalkyl, and methyl phenyl ketones and the free energies of activation for oximation of the same ketones. This suggests that decomposition of the Criegee intermediate is rate determining.[23]

Baeyer–Villiger reaction rates generally are not those expected for rate-determining carbonyl addition. Cyclohexanone reacts 200 times slower with peracetic acid than with TFPAA using trifluoroacetic anhydride catalyst in ethylene chloride at 30°. Since the weakly nucleophilic TFPAA should be less reactive than peracetic acid toward carbonyl addition, the observed rate difference strongly favors rate-determining decomposition of the Criegee intermediate.[15]

Electron withdrawal on the leaving group facilitates the rate-determining migration step as indicated by the small positive values [ρ = 0.2–0.4 (σ)] noted for the oxidation of benzaldehyde with substituted perbenzoic acids at pH < 9.[12] Acid catalysis also facilitates loss of the leaving group at low pH.[12,23–27]

Electron-donating groups on the migrating group facilitate the rearrangement. Rate data for TFPAA oxidation of *p*-substituted acetophenones in acetonitrile or ethylene chloride[23] and peroxomonophosphoric acid (PMPA) in acetonitrile[28] plotted versus substituent values give similar negative ρ values (ρ = −1.45, −1.10, and −2.55). For Hammett plots of the kinetic data for MCPBA oxidation of the same substrates in chloroform, a better linear fit is observed with (ρ = −1.36).[17] Peroxomonosulfate (PMSA) oxidations of substituted aryl aldehydes also show a negative value (ρ = −1.70),[26] and negative ρ values [−5.7 and −3.8 (σ^+)] were revealed for aryl migration of substituted benzaldehydes in acidic and neutral media.[12] Carbonyl addition reactions normally give moderate positive ρ values;[23] the negative ρ values are consistent with an activated complex which is electron deficient on the migrating group during the rate-determining step 2.

Caution must be exercised in using reaction ρ values to interpret mechanisms, since the equilibrium constant for formation of the Criegee intermediate prior to the rate-determining migration step affects the observed rate data. Hammett results cannot be explained straightforwardly at moderate acidity, but stronger peracids cause fast equilibrium formation of the Criegee intermediate and give clearer kinetics.[29]

Rate-Determining Addition

Rate-determining addition (Step 1 of Eq. 1) has been postulated for aryl aldehydes and ketones substituted with strongly electron-donating groups. For MCPBA oxidation of *p*-methoxyacetophenone a negligible carbon isotope effect $k_{12}/k_{14} = 0.998$ was observed. If there is no equilibrium isotope effect for addition of peracid to the ketone carbonyl,[16] the absence of an isotope effect is consistent with rate-controlling addition of peracid to the ketone carbonyl.[17]

Evidence suggests rate-determining addition to carbonyl for the perbenzoic acid oxidation of *o*- and *p*-hydroxybenzaldehydes in aqueous ethanol. For *p*-methoxybenzaldehyde migration appears to be rate determining above pH 5, whereas the apparent rate below pH 5 is controlled by both addition and migration.[12] In benzene and ethanol solvents migration appears to be rate determining.[29]

A rate-determining addition step 1 (Eq. 1) has been suggested for acid-catalyzed reactions of peroxymonophosphoric acid in aqueous acetic acid with several cyclopentanones and cyclohexanones on the basis of reactivity, activation energy and entropy values, solvent, and catalyst effects.[25] Rate-determining addition occurs in the oxidation of biacetyl and benzil with peroxomonosulfuric acid and peroxomonophosphoric acid; these reactions are not acid catalyzed, and reaction rates increase with a rise in pH.[30] By contrast, rate-determining migration step 2 (Eq. 1) is suggested by $\rho = -2.55$ (σ) for the peroxomonophosphoric acid oxidation of substituted acetophenones in acetonitrile.[28] Also, similar activation energy data for peroxomonosulfate oxidation of dialkyl ketones in aqueous acetic acid have been used to support rate-determining rearrangement step 2.[24]

Oxidation of the 1,2-diketone *o*-quinone with isotopically labeled hydrogen peroxide under basic conditions indicates that the normal two-step Baeyer–Villiger mechanism is followed for C–C bond cleavage.[31] It is notable that Hammett correlations of the reactions of substituted benzils indicate the limitations inherent in the use of the sign of ρ values for the assignment of mechanism. For a reaction with a rapid preequilibrium step followed by a slower migration, the observed rate depends on both the equilibrium constant for formation of the Criegee intermediate and the rate of the migration step (Eq. 2).[32] The noncatalyzed rearrangement of substituted benzils with peracetic acid in acetic acid has a $\rho = +1.51$ (σ), while the sulfuric acid catalyzed rearrangement has a $\rho = -0.67$ (σ). The change in sign may be consistent with rate-determining addition in both cases. The positive ρ in the absence of catalysts reflects the ability of electron-withdrawing groups to facilitate attack by nucleophilic peroxide oxygen on the carbonyl group. The negative ρ with acid catalysis is postulated to reflect an increase in the value of the equilibrium constant K as electron donation facilitates protonation of the benzil (Bz_2) carbonyl group.[33]

Similar arguments might be made to support migration in the adduct as rate-determining.

$$Bz_2 + H^+ \overset{K}{\rightleftharpoons} Bz_2H^+$$

$$Bz_2H^+ + AcO_2H \xrightarrow{k} \text{Adduct} \qquad \text{(Eq. 2)}$$

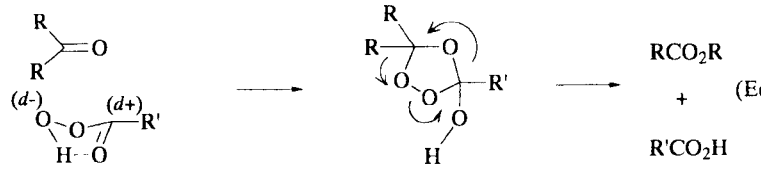
$$[Bz_2H^+] = K[H^+][Bz_2]$$

$$\text{rate} = k[Bz_2H^+][AcO_2H] = kK[H^+][Bz_2][AcO_2H]$$

Alternative Mechanisms

Exceptions to the above generalizations of a two-step ionic mechanism with step 2 migration as rate determining have been suggested. Although a plot of the trifluoroacetic anhydride catalyzed oxidation of *p,p'*-substituted benzophenones in refluxing methylene chloride versus σ^+ is linear with a $\rho = -0.77$, supporting the ionic mechanism, when peracetic acid is the oxidant there is not a Hammett plot correlation. The relative rate results in Table 1 for these oxidations fit the rate at which aryl radicals attack aromatic rings. Although a mechanism involving a carboxylate radical is implicated under this set of conditions, no carbon dioxide evolution is observed.[34]

A concerted 1,3-dipolar mechanism has been suggested (Eq. 3).[35] It has been used to rationalize rate law data for the peroxymonophosphoric acid (PMPA) oxidation of cycloalkanones.[25] The results of ^{18}O-tracer experiments implicate dioxiranes as intermediates in the oxidation of cyclohexanone and acetophenone with bis(trimethylsilyl)peroxomonosulfate.[36]



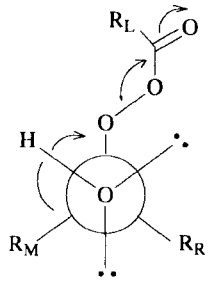
(Eq. 3)

TABLE 1. RELATIVE RATE DATA FOR OXIDATION OF *p,p'*-UNSYMMETRICALLY SUBSTITUTED BENZOPHENONES

	Peracid	
Substituent	TFPAA	PAA
OCH_3	211	152
CH_3	26	9
NO_2	1	3.2
Br	14	2
Cl	12	1.2
H	—	1

Stereoelectronic Effects

Stereoelectronic requirements proposed for the migration step are antiperiplanar arrangements between both a nonbonding electron pair on oxygen and the O–O bond with the bond of the migrating carbon atom as in **6**.[9,37–40] These prerequisites and considerations of nonbonded steric interactions between R and hydroxy hydrogen have accounted for the observed preference of C-2–methylene migration from conformer **7**.[38,40]



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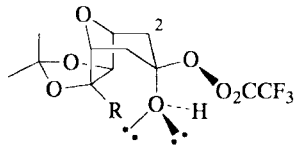
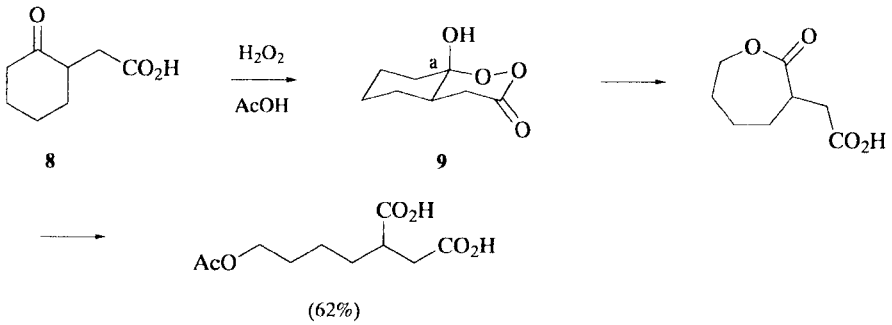


7

Evidence for a stereoelectronic effect in an intramolecular Baeyer–Villiger reaction was found in the preferential migration of the methylene carbon during oxidation of cyclohexanone **8**. Assuming rearrangement occurs from the rigid *trans*-fused intermediate **9**, only bond **a** can assume the proper antiperiplanar orientation for migration.[37]



(62%)

SCOPE AND LIMITATIONS

Reactions of Straight-Chain Ketones

Oxidation of Dialkyl Ketones. Migratory ability of alkyl groups in acid catalyzed Baeyer–Villiger reactions decreases in the orders tertiary > secondary > primary > methyl,[15,41–44] and benzyl > primary > methyl.[16,21] Migratory aptitudes of cyclopropyl ketones with MCPBA or TFPAA are phenyl = secondary > pri-

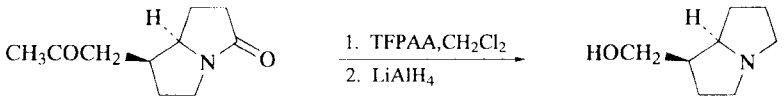
mary > cyclopropyl > methyl.[42,45] Ketones of the type RCH_2COCH_2R, which have only primary alkyl groups attached to carbonyl, are unreactive with perbenzoic acid and peracetic acid,[46] but they do undergo oxidation with the reactive trifluoroperacetic acid,[42] bis(trimethylsilyl)monoperoxysulfate,[47] potassium persulfate in sulfuric acid,[41] and with 90% hydrogen peroxide/boron trifluoride etherate.[46] A method for preparation of α-deuterated acids and alcohols which avoids the use of deuteride reducing agents involves catalyzed deuterium exchange alpha to carbonyl and then cleavage with TFPAA (Eq. 4).[48,49]

$$CH_3CD_2COCD_2CH_3 \xrightarrow{\text{TFPAA}} \underset{(64\%)}{CH_3CD_2CO_2H} + CH_3CD_2OH \qquad \text{(Eq. 4)}$$

The migratory trend in Baeyer–Villiger oxidations has been attributed to electronic and conformational factors. Groups which can best support a positive charge by induction or hyperconjugation are more likely to migrate. It has also been suggested that migration occurs from a favored rotamer **10**, which has the bulkier group antiperiplanar to the leaving group.[15]

10

Since methyl is a poor migrator, the Baeyer–Villiger reaction has been used extensively to convert methyl ketones to acetate esters while shortening a carbon chain by two units.[50–54] The method is of broad utility, since methyl ketones can be derived from carboxylic acids[55–60] and methyl-substituted olefins.[50,61–64] The Baeyer–Villiger oxidation was utilized to shorten the carbon chain in a synthesis of the alkaloid isoretronecanol (Eq. 5).[65]

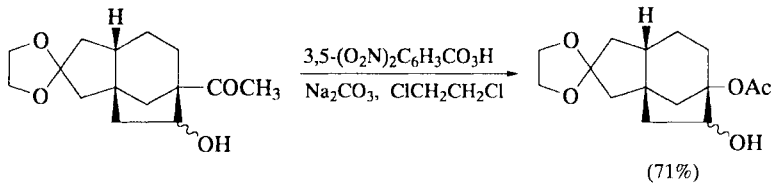


(48%)

(Eq. 5)

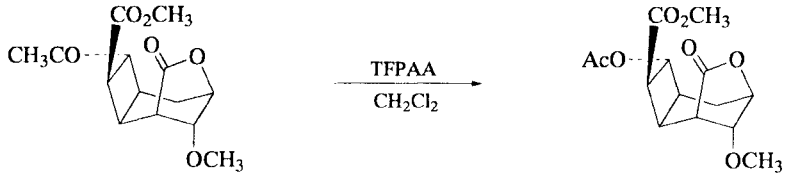
Baeyer–Villiger oxidation of methyl ketones has played a major role in a number of novel synthetic transformations. Examples include the introduction of a bridge-

head hydroxy group following use of an acetyl functionality in an aldol condensation in the synthesis of gibberellic acid (Eq. 6).[66] The Woodward reserpine precursor



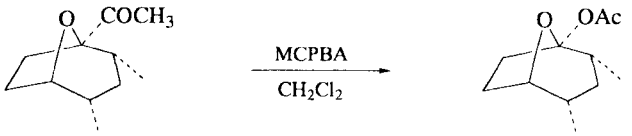
(Eq. 6)

12, the acetate of a β-hydroxyester required for a ring-cleavage reaction, was prepared from the β-acetyl compound **11**.[67]

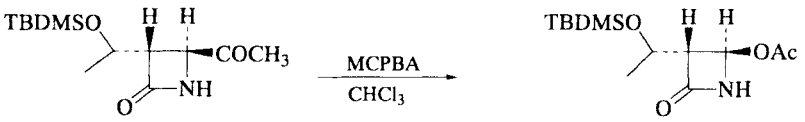


11 **12** (59%)

Ether or alcohol oxygen,[61,68–72] and amine[73] or, less effectively, acylated nitrogen[74] atoms alpha to the carbonyl aid migration and accompanying chain cleavage during peracid reactions. MCPBA oxidation of the acetylfuran derived cycloadduct **13** provided the acetate of a 4-hydroxycycloheptanone hemiketal **14** needed in a stereocontrolled strategy for synthesis of the Prelog–Djerassi lactone and similar macrolide antibiotics.[75] Oxidation of the acyl β-lactam **15** was part of a synthesis of the penam and carbapenem intermediate **16** from D-allothreonine and *trans*-crotonic acid.[55]



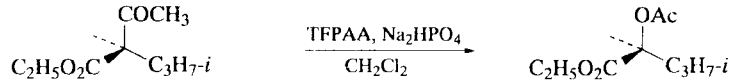
13 **14** (60%)



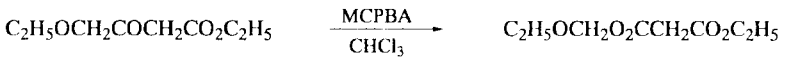
15 **16** (90%)

Peracid treatment of acyclic 1,3 diketones can give complex reaction mixtures from α-hydroxylation,[76] cleavage of both acyl groups,[76,77] and molecular rearrangements.[78,78a]

However, the α-acyl ester **17**, which lacks an acidic methylene hydrogen, can be converted to an α-acetyl ester with TFPAA.[79] Reaction of peracid with the enol form of a 1,3-dicarbonyl compound is suppressed by the α-directing ether substituent in ethyl 4-ethoxy-3-ketobutyrate, and diester **18** is obtained with MCPBA.[79a]

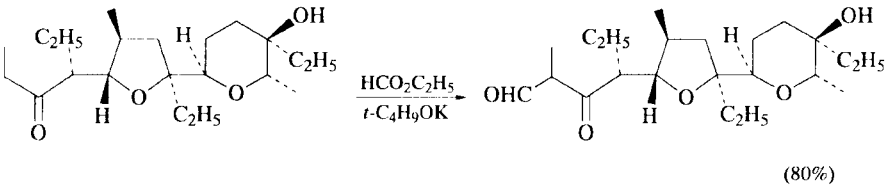


17 (89%)

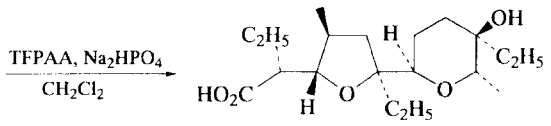


18 (70-80%)

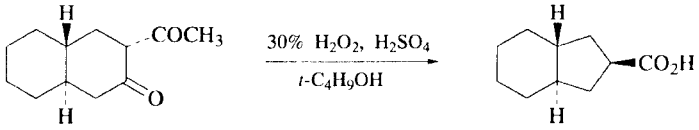
A novel method of directed chain shortening by an α substituent involves initial introduction of a formyl group alpha to a ketone and subsequent oxidation with TFPAA (Eq. 7).[80] Acidic 30% hydrogen peroxide treatment of an α-acetyl cyclic ketone results in a ring-contracted carboxylic acid (Eq. 8).[81,82]



(80%)

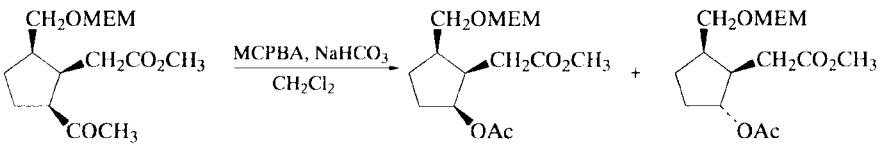


(79%) (Eq. 7)



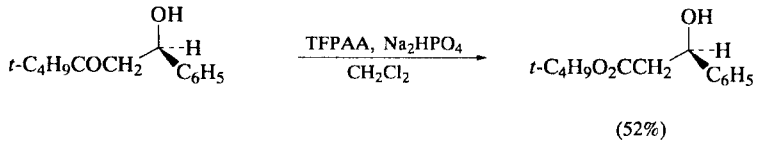
(81%) (Eq. 8)

A rare example of partial epimerization of acetyl prior to oxidation has been observed for the sodium bicarbonate catalyzed MCPBA reaction with the hindered cyclopentyl substrate **19**. A mixture of *cis* and *trans* acetates was isolated. The *trans*-acetyl isomer of **19** reacts normally.[83]



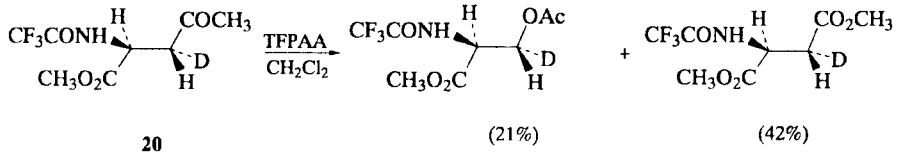
19 (9%) (42%)

Complementary to the use of methyl as a nonmigrating group is the use of *tert*-butyl as a preferentially migrating ligand.[84] Normally, oxidation of β-hydroxy methyl ketones gives preferential migration toward the hydroxy group to form 1,2-diol monoesters.[85] However, β-hydroxy *tert*-butyl ketones oxidize to *tert*-butyl esters of β-hydroxycarboxylic acids (Eq. 9).[86]



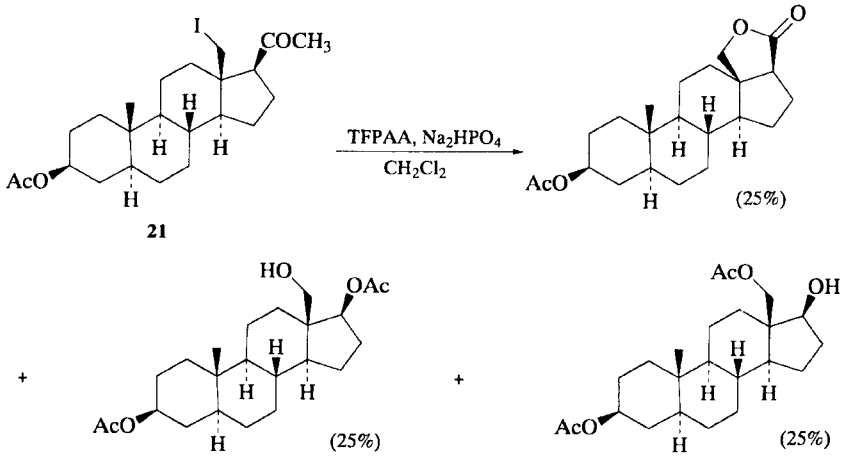
(Eq. 9)

The bias against methyl migration has been overcome when migration of one group is retarded. In the oxidation of aminoester **20** the strongly electron-withdrawing ester and *N*-acyl groups decrease the migratory ability of the proximate methylene (67:33 bias for methyl migration).[87–90]

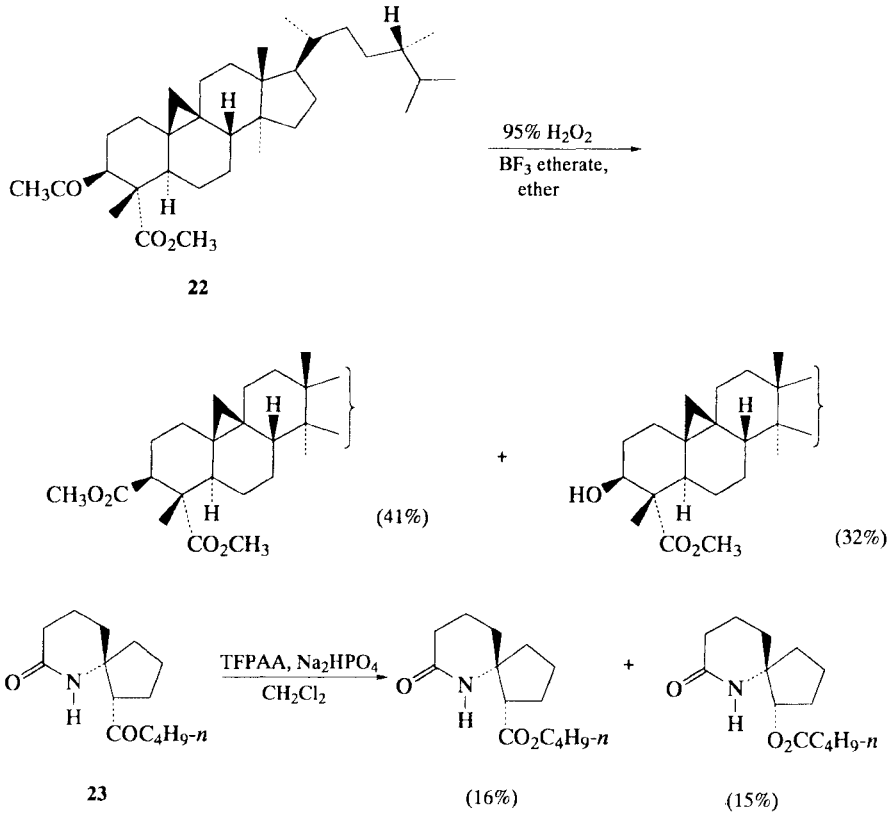


20

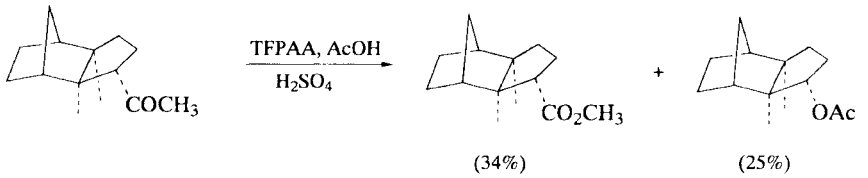
Significant amounts of methyl migration have been observed even when the competition is with a secondary alkyl group. Examples include the oxidations of 18-iodo-20-ketosteroid **21** (1:2 methyl:secondary carbon migration)[91] and 3-acetyl-4-methoxycarbonyl steroid **22** (41:32 methyl:secondary carbon migration.[51] Primary alkyl migrates in preference to secondary alkyl in the spiro-amide **23**.[92]



21



Migration of the smaller group is a likely consequence of substituent electron-withdrawing effects, since conformational considerations should have resulted in migration of the bulkier group in these highly crowded substrates.[15] Nevertheless, there is one example in which crowding favors methyl migration (Eq. 10).[93]



(Eq. 10)

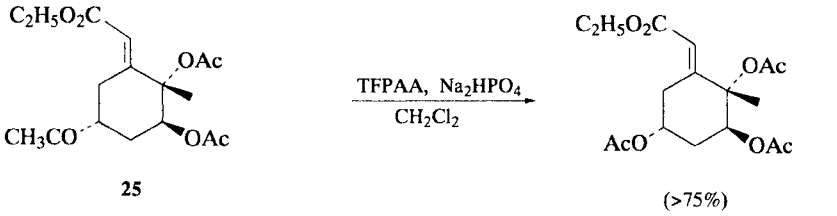
Migration can be enhanced by a β-silicon substituent, and the proximal primary alkyl group of **24** migrates in preference to the distal secondary one. The migratory aptitude of β-trimethylsilylethyl is intermediate between that of secondary and tertiary alkyl groups.[94]

$(CH_3)_3Si(CH_2)_2COC_3H_7$-*i* $\xrightarrow[CH_2Cl_2]{MCPBA,\ Na_2HPO_4}$ $(CH_3)_3Si(CH_2)_2O_2CC_3H_7$-*i* (53%)

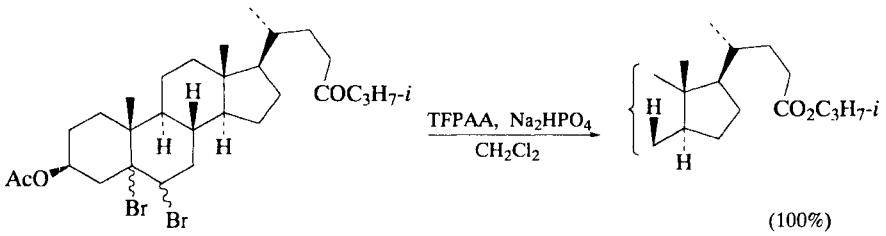
24

\+ $(CH_3)_3Si(CH_2)_2CO_2C_3H_7$-*i*(27%)

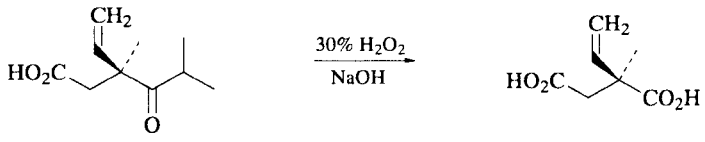
Chemoselective Baeyer–Villiger oxidations can occur in the presence of amino acids,[95,96] amines,[97] pyridines,[98,99] or anilines.[97] However, 3-acetylpyridine forms only the *N*-oxide with MCPBA.[100] Chemoselectivity in the presence of olefins depends upon structure and oxidizing agent. Chemoselective olefin oxidation of nonconjugated acyclic enones with organic peracids is generally faster than the Baeyer–Villiger reaction.[101–104] Electron-poor olefin **25** undergoes a Baeyer–Villiger reaction with TFPAA.[105] A reactive double bond can be protected as its dibromide, as in the oxidation of the steroid **26**.[104] Basic hydrogen peroxide, which doesn't attack isolated olefins, cleaves the isopropyl group of **27** in preference to the tertiary substituent bearing a carboxylate anion.[106]



25 (>75%)



26 (100%)



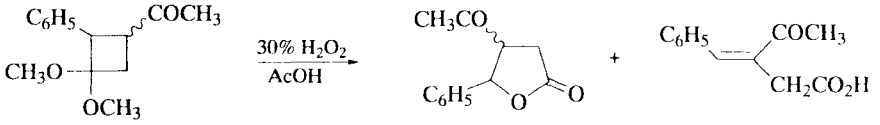
27 (100%)

Carbonyl group selectivity is observed for MCPBA oxidation of a side chain acetyl in preference to a hindered ring carbonyl in cyclic ketone **28**[107] and hindered 11-ketosteroids.[108,109] However, the ring carbonyl of **29** reacts.[110] Deketalization of

30 and peracetic acid oxidation of the derived cyclobutanone occurs in preference to oxidation of the side-chain acetyl.[111]

28 (77%)

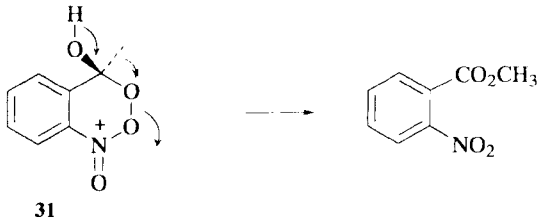
29 (79%)



30 (95%)

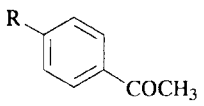
Oxidation of Aryl Alkyl Ketones. Aryl alkyl ketones can undergo Baeyer–Villiger oxidation with migration of either substituent depending upon the functional groups on the aryl ring, structure of the alkyl group, and choice of oxidizing reagent and conditions.[2] Relative migratory aptitudes for phenyl alkyl ketones using buffered TFPAA are tertiary > secondary = benzyl > phenyl > primary > methyl.[15,112]

Substituents on an aryl group slightly decrease the amount of aryl migration as shown in Table 2.[15,28,29,113] The large preference for methyl migration over an *o*-nitrophenyl group could be related to partial participation by nitro group oxygen in cleavage of the O–O bond to form an intermediate peroxide **31**. The methyl group, but not the aryl ring, can achieve the proper *anti* alignment required for the migration step.[113]



31

TABLE 2. TFPAA OXIDATION OF SUBSTITUTED ACETOPHENONES

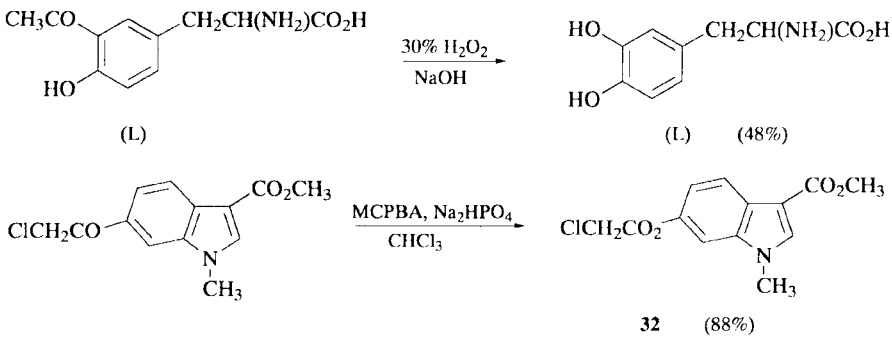


Substituent R	Aryl Migration (%)	Yields (%)	Ref.
p-NO_2	87	67	15, 113
m-NO_2	63	100[a]	113
o-NO_2	6	38	113
H	100	100	113
Cl	97	36	15
CF_3	82	73	113
CO_2H	97	86	113
CO_2CH_3	97	77	113
OCH_3	88	75[a]	113

[a]The yield was determined by titration.

Weaker peracids afford greater reaction regioselectivity. For phenyl cyclohexyl ketone the weaker peracid peracetic acid (10% phenyl migration) is more selective for aryl migration than is TFPAA (20% phenyl migration).[15] Sodium perborate is selective solely for aryl migration with *p*-methoxy-, *p*-bromo-, *p*-phenyl-, or *p*-methylacetophenone.[114] Steric effects have been studied for the Dakin oxidation of *o*- and *p*-acylphenols with hydrogen peroxide/sodium hydroxide. Larger alkyl groups on the carbonyl slow the reaction.[115]

The preference for aryl over primary alkyl migration allows acylated aromatic rings to be converted to phenols.[116,117] The oxidation of a C-2 acyl group on an aromatic A-ring is chemoselective in the presence of a steroidal 17-ketone.[118,119] A two-step procedure of acylation followed by Baeyer–Villiger oxidation has been used to convert L-tyrosine to L-dopa (Eq. 11).[95] It was necessary to use the chloroacetyl group in order for the Baeyer–Villiger reaction to proceed as desired to prepare the oxygenated indole ring **32**.[120,121]



(L) (L) (48%)

32 (88%)

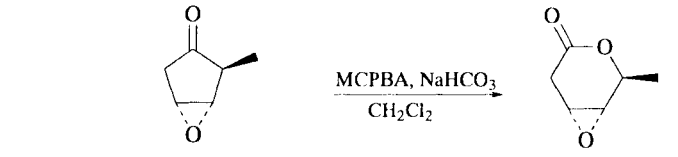
(Eq. 11)

When oxidations of acetophenones are carried out using *tert*-butylhydroperoxide/potassium hydroxide in chlorobenzene, benzoic acids derived from preferential primary, secondary, or tertiary alkyl migration are obtained rather than phenols. Unlike the peracid mediated Baeyer–Villiger oxidation, electron-withdrawing substituents on the aryl ring increase the reaction rate. Diaryl ketones do not undergo the oxidation. The reaction does not involve radicals since there is no induction period and no inhibition by the radical scavenger arsenious acid.[122-124]

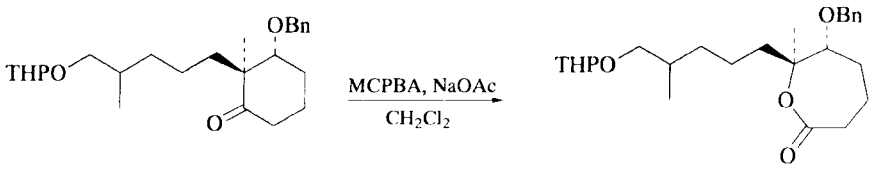
Oxidation of Diaryl Ketones. In the cleavage of unsymmetrical diaryl ketones the more electron-releasing group normally migrates.[2] With mono-*p*-substituted benzophenones the migratory order is H > Br > Cl > NO_2.[20] An *ortho* effect has been noted; *p*-chlorophenyl migrates in preference to an *o*-chlorophenyl, and an *o*-methylphenyl hinders migration relative to phenyl. An *o*-methoxyphenyl group still migrates preferentially.[125] A dibenzocyclobutane migrates in preference to phenyl.[126,127]

Reactions of Monocyclic and Spirocyclic Ketones

Oxidation of cyclic ketones to lactones is useful in the synthesis of heterocycles as shown by the formation of **33**, a precursor of the carbohydrate daunosamine,[128] and **34**, a precursor of the cyclic ether ring of zoapatanol.[129]

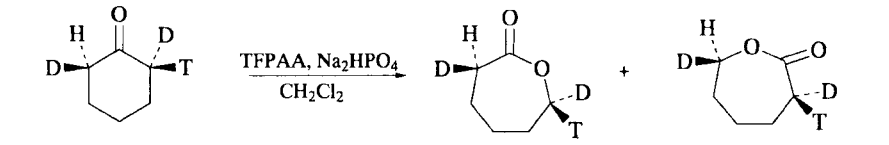


33 (98%)

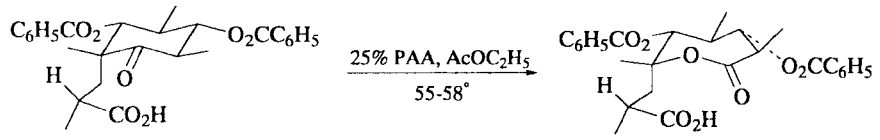


34 (70%)

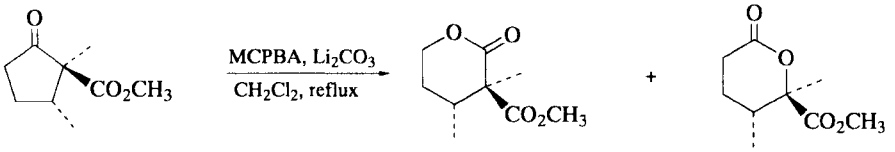
An extensive use of the Baeyer–Villiger reaction is in the stereocontrolled synthesis of carbon chains by ring opening of the lactones derived from stereoselectively functionalized cyclic ketones.[130-142] By this method chiral 2-deuterio-2-tritioacetic acid was synthesized from the chiral ketone **35**.[143] In the total synthesis of erythronolide **B** regioselective ring opening of a substituted cyclohexanone **36** provided the hydroxyacid precursor **37**,[144] and a stereocontrolled synthesis of the diester side chain of integerrinecic acid used the major isomer **39** formed upon oxidation of the cyclopentanone **38**.[145]



35 (>85% of the mixture)



36 37 (70%)



38 (13%) (77%)

39

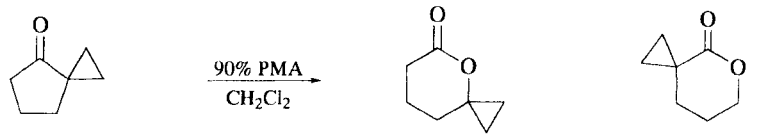
Cyclobutanones are especially reactive and can be ring expanded not only with customary organic peracids,[146] but also with hypochlorous acid[147] or alkaline hydrogen peroxide at room temperature.[148] Rates of oxidation of some cyclic ketones with perbenzoic acid are shown in Table 3.[149] The effect of bulky substituents near the carbonyl is to lower the rate by decreasing the equilibrium constant for formation of the Criegee intermediate (Eq. 1). Steric effects account for the selective oxidation of the side-chain carbonyl in ketone **28**,[110] but the ring ketone in the *trans*-monomethyl

TABLE 3. OXIDATION OF SELECTED KETONES WITH PERBENZOIC ACID (25°, CHLOROFORM)

Ketone	Rate ($k \times 10^{-4}$ L mole^{-1} s^{-1})
Cyclopentanone	2.2
3-Methylcyclopentanone	1.4
Cyclohexanone	15.8
2-Methylcyclohexanone	7.5
2,2-Dimethylcyclohexanone	5.0
3-Methylcyclohexanone	12.2
4-Methylcyclohexanone	19.2
4-*tert*-Butylcyclohexanone	27.7
2-Chlorocyclohexanone	0.4
Cyclodecanone	0.1

ketone **29**.[107] The oxidation rate for the medium ring cyclodecanone is retarded relative to the rates for cyclohexanone or cyclopentanone.

The regiochemistry of oxygen insertion follows the principles set out for oxidation of open-chain ketones. There is a customary preference for migration of the α substituent which has the most alkyl substituents. This is true for ring sizes of four,[146,150–153] five,[128,133,134,154–166] six,[110,129,135,137,138,140,167–173] seven,[174] nine,[131] and twelve carbons.[175–178] An α-phenyl group facilitates migration,[179–182] as do α-benzyl[183] and α-allyl groups.[102,120,130,184] In contrast to the preference in open-chain ketones, the major product **41** isolated in the permaleic acid (PMA) oxidation of **40** is formed by migration of the spirocyclopropyl carbon.[185] The spiro carbon also migrates in α-spirocyclobutanones,[148,186–193] even if electron-withdrawing β-bromo,[194] β-hydroxy,[194,195] or β-*tert*-butyldimethylsilyloxy[194,195] groups are present on the adjacent ring.



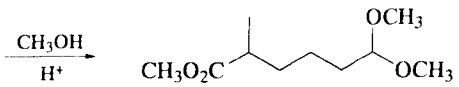
40 **41** **42**

41:**42** = 89:11

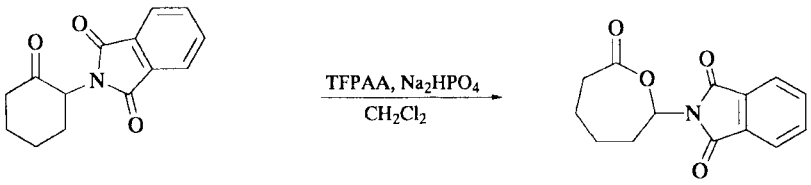
Steric hindrance toward attack by peracid on the carbonyl group can stop oxidation. Although 2-chloro-2,4,4-trimethylcyclobutane-1,3-dione reacts with peracetic acid, no reaction occurs if the 2 methyl is replaced by isopropyl.[153] The medium ring compound cyclodeca-1,6-dione is unreactive with MCPBA after 31 days at 25° or 45 hours at 45°.[196]

Migration is favored by α-ether[197,198] and α-acetate[199,200] groups, and an α-trimethylsilyloxy group directs migration in preference to a methyl group in **43**.[197] An α-*N*-methyl-*N*-tosyl group[198a] is directing in the same manner as the imide group is directing in the oxidation of **44**,[201] while the α-amino group of **45** facilitates cleavage of the ring.[73] An α-chloro group normally retards migration.[153] If TFPAA is the oxidant, 2-chlorocyclohexanone gives an α-chlorolactone,[201] but adipic acid, which arises by cleavage at the chlorine bearing carbon, is formed using perarsenious acid on polystyrene.[182]

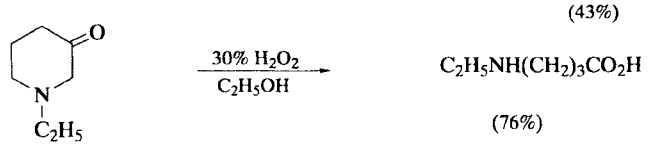
43



(50-60%)

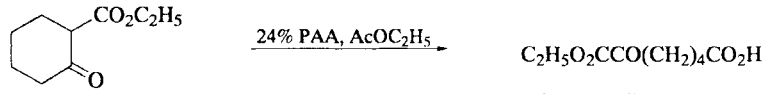


44 (43%)



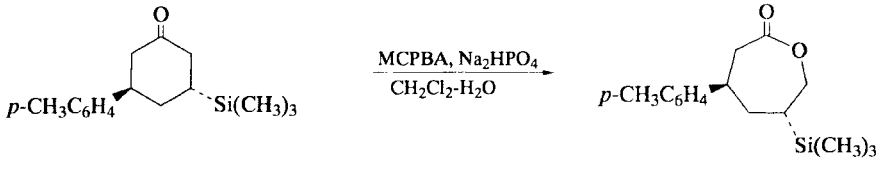
45

Cyclic α-acyl ketones undergo ring contraction and ring cleavage reactions with neutral or basic hydrogen peroxide;[78,202-204] Peracetic acid converts **46** to **47**.[205] The electron-withdrawing α-ester substituent in **38** does not block regioselective Baeyer–Villiger oxidation toward the alkyl group to give **39**.[145,206]

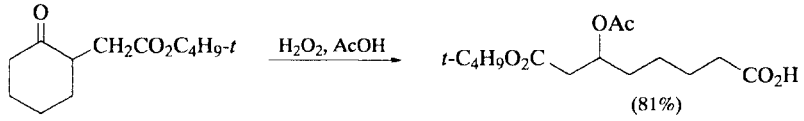


46 **47** (80%)

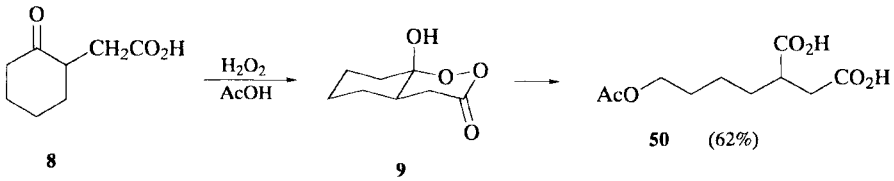
The directing effect of a β-trimethylsilyl group[139,207] is impressive as shown by the totally regioselective formation of lactone **48**.[208,209] Silyl lactones are useful in the synthesis of olefinic esters and acids.[94] A β-alkoxycarbonyl substituent does not retard migration of the proximal alpha carbon in the peracetic acid oxidation of ketone **49**.[37] The β-carboxylic acid in ketone **8** effects an intramolecular Baeyer–



48 (94%)

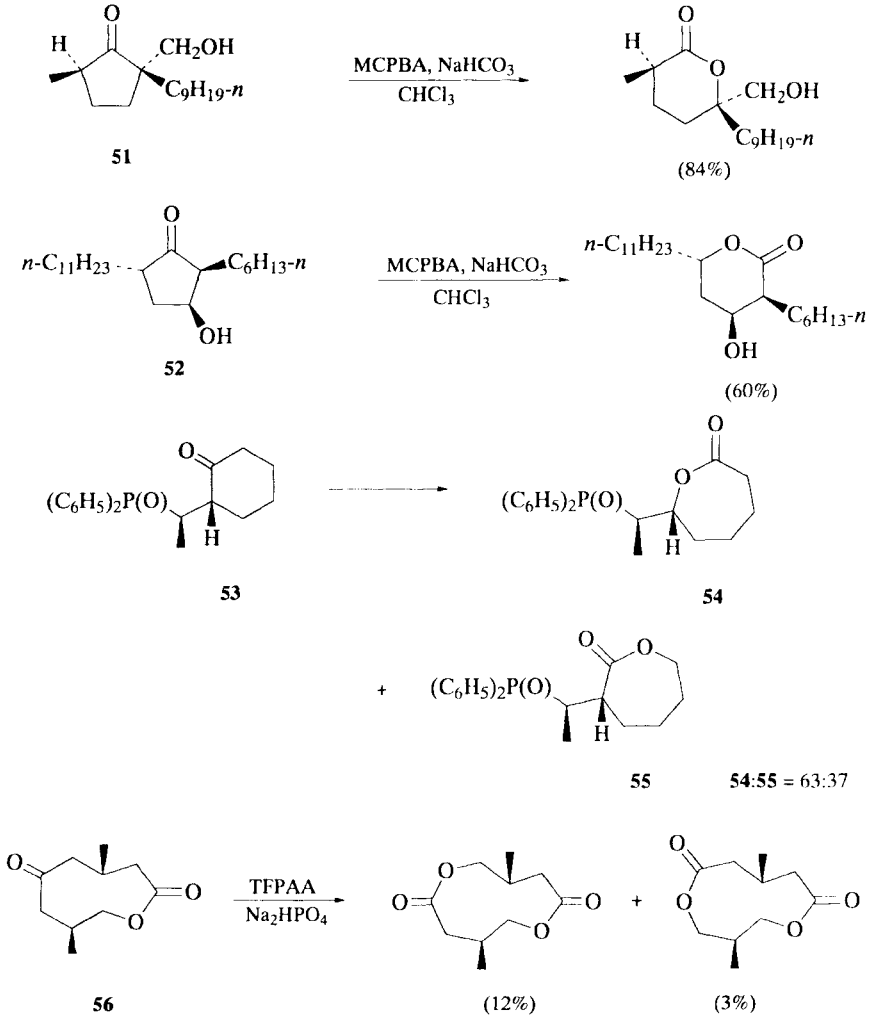


49

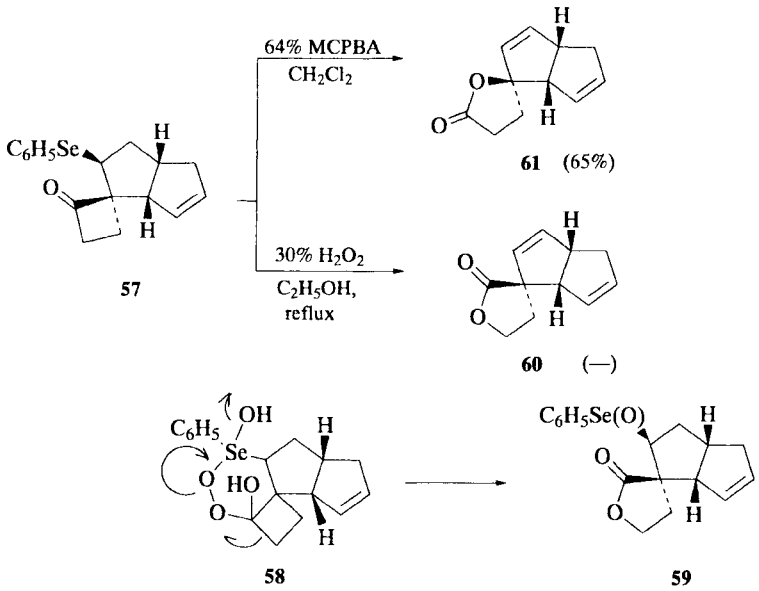


8 **9** **50** (62%)

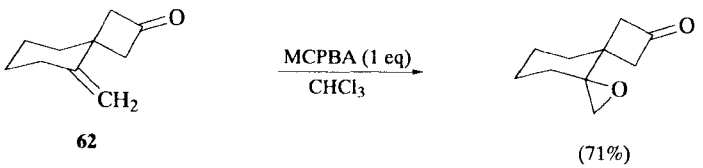
Villiger reaction via **9** to give **50**; only the distal methylene in **9** can assume the proper orientation for migration.[37] Oxidation of the *tert*-butyldiphenylsilyl ether of α-hydroxymethylcyclopentanone[209a] and ketone **51** with MCPBA both occur with migration toward the β-hydroxy group,[166] while β-hydroxyketone **52** gives solely lactone derived by migration of the methine away from the β-hydroxy group.[209b] Hydrogen peroxide results in β-elimination and cleavage of 2-aminomethylene ketones at the 2 position,[158] but oxidation can proceed further as in the conversion of 2-isopropoxymethylcyclohexanone to adipic acid.[204] The directing effect of a β-phosphine oxide group on a C-2 alkyl side chain of **53**, although oxidation results in major C-1 migration to give **54**, is affected by the stereochemistry of a methyl group at C-1.[210] The methyl epimer of **53** gives 96% insertion adjacent to the side chain. The combined influence of α-carbonyl and oxygen substituents in ketolactone **56** results in preferential migration of the carbon away from oxygen.[211]



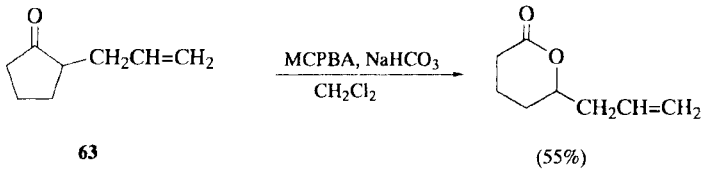
A neighboring β-selenium substituent influences the regiochemistry of oxidation of the spirocyclobutanone **57**. With hydrogen peroxide in ethanol initial oxidation to selenoxide enables formation of a cyclic peroxide **58**. Geometric constraints force migration of the methylene group to give **59** and then lactone **60**. When hydrogen peroxide/potassium carbonate,[212] for which Baeyer–Villiger oxidation is faster than selenium oxidation, or MCPBA, which cannot form a cyclic peroxide, are used as oxidants, the usual bridgehead migrated lactone **61** is obtained.[195,213]



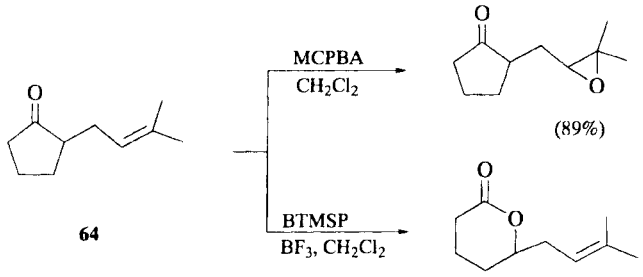
Chemoselective oxidations of α-thioether[214,215] and α-phenylselenenide[216] ketones occur on the heteroatoms. Vinylsilanes form epoxysilanes[217] and α-diazoketones form 1,2-diketones with MCPBA.[218] Chemoselectivity favoring Baeyer–Villiger reaction for nonconjugated enones depends upon the relative reactivities of the carbonyl and olefin and the choice of oxidant.[184] Reactive four-membered rings undergo only ring expansion with 30% hydrogen peroxide/sodium hydroxide.[148,187,195,212,213] Ring expansion is also generally found with cyclobutanones and organic peroxides;[151,187,195,213] however, oxidation of spirocyclobutanone **62** is an exception.[219]



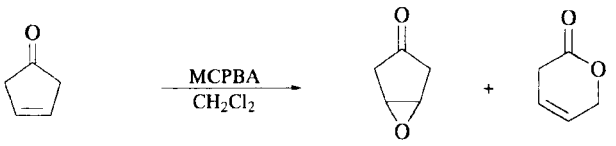
Allylcyclopentanone **63** undergoes Baeyer–Villiger oxidation with MCPBA.[130] Although the dimethylallylcyclopentanone **64** reacts preferentially on the double bond with MCPBA, bistrimethylsilyl peroxide (BTMSP) with boron trifluoride



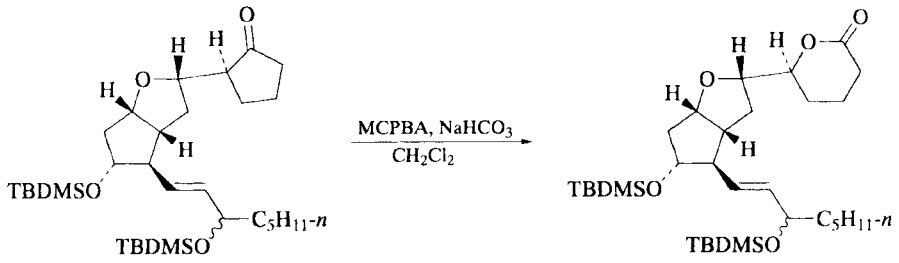
63 (55%)



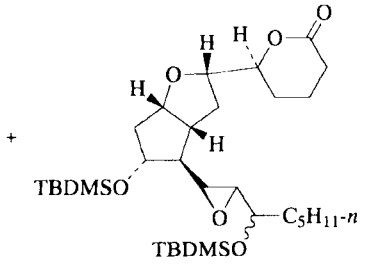
64 **65** (44%)



66 (63%) (6%)

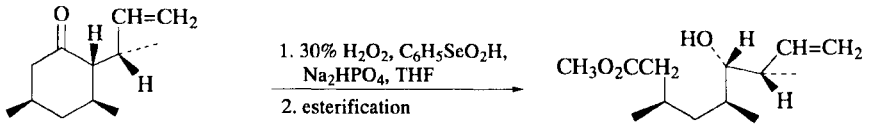


67 (81%)



(14%)

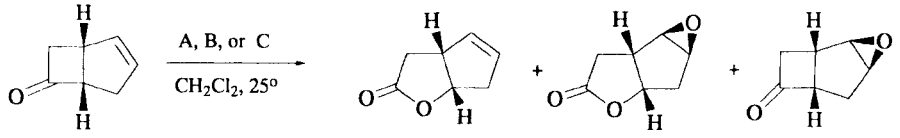
catalyst affords the lactone **65**.[220] Cyclopentenone **66** also affords mainly epoxide with MCPBA.[221] It has been postulated that steric hindrance provided by an allylic *tert*-butyldimethylsilyloxy group hinders epoxidation and favors Baeyer–Villiger oxidation of ketone **67**.[161] Although 2-allylcyclohexanone undergoes Baeyer–Villiger reaction with peracetic acid,[184] it is necessary to use perseleninic acid to carry out the ring cleavage of ketone **68**.[222]



68 (63%)

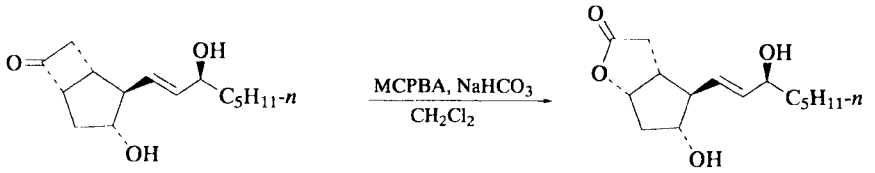
Reactions of Fused-Ring Ketones

Oxidation of Alicyclic Ketones. Cyclobutanones are reactive under a variety of Baeyer–Villiger conditions, and chemoselective oxidations in the presence of cyclohexanones can be affected with peracetic acid[111] or basic *tert*-butyl hydroperoxide.[223] Lactone formation in the presence of olefins often can be carried out with hydrogen peroxide/acetic acid[224,225] or limited amounts of organic peracids.[226–229] Reaction of MCPBA, which gives high Baeyer–Villiger selectivity with ketone **69**,[230] provides the prostaglandin precursor **70**.[231] Although not always effective in carrying out the Baeyer–Villiger oxidation,[232] a better method to avoid olefin epoxidation is to use basic hydrogen peroxide[233] or alkyl peroxide solutions,[234] as in formation of the lactone **71**, an eriolanin and eriolangin precursor.[235] Basic hydrogen peroxide is effective for oxidation of a cyclobutanone even in the presence of a conjugated ketone.[187,236]

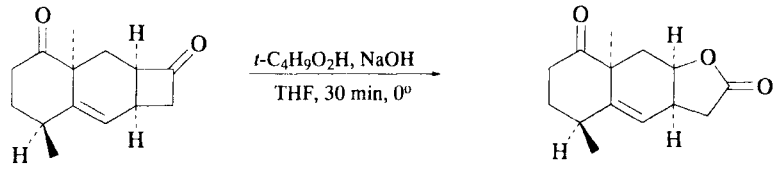


69

	I	II	III
A = MCPBA	(95.3%)	(2.8%)	(1.4%)
B = $Cl_3CCH_2CO_3H$	(28%)	(41%)	(31.3%)
C = $C_2H_5OCO_3H$	(69%)	(21%)	(9.4%)



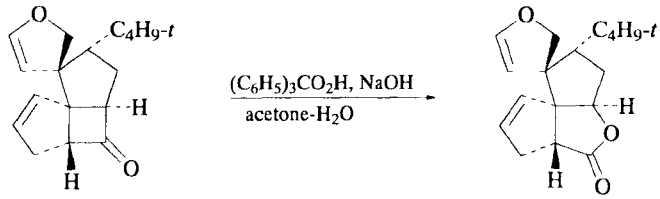
70 (86%)



71 (83%)

The regiochemistry of oxidations of fused-ring cyclobutanones is usually toward the bridgehead.[237] However, nonbridgehead substitution in the cyclobutanone ring by α-*N*-methyl-*N*-tosyl or α-methoxy substituents directs oxygen insertion regiospecifically toward the substituent.[198a] Similar attachment of an alkyl group[238] or even a halogen,[239] which in steroids often retards migration of the attached carbon,[240,241] leads to formation of regioisomeric mixtures. A bridgehead will migrate in preference to a cyclopropyl,[238] or an α-carbon substituted by an alkyl and a halogen.[242] Several cyclobutanones fused to bridged rings react with basic hydrogen peroxide to give preferentially methylene migrated lactones.[243,244]

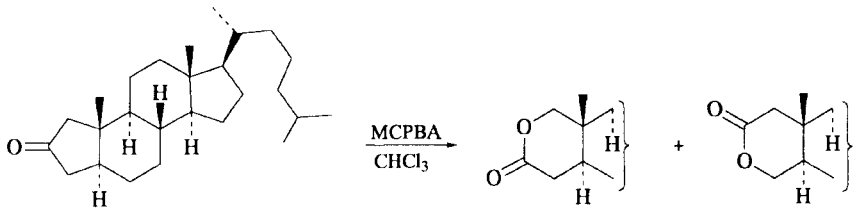
Cyclobutanone oxidations are integral reactions for syntheses of prostaglandins,[231,233,237,245] lactone-annelated steroids,[246] α-methylene-γ-lactones,[226,238] and paniculide A.[247,248] The lactone ring of ginkolide B intermediate **72** is introduced in a regioselective and chemoselective fashion using basic triphenylmethyl hydroperoxide.[249,250]



72 (86%)

Fused-ring cyclopentanones in which the carbonyl is adjacent to a bridge position or an alkyl substituent react with organic peracids to give migration of the more substituted carbon.[251-253] Such oxidations are utilized as part of an approach to cyclohexenones[254] and in syntheses of the lactone moieties of the klaineanone ring system of quassinoids,[255,256] xylomollin,[257] and lineatin.[258,259] Lactone ring openings of substituted fused five-membered rings are involved in stereocontrolled syntheses of sesquifenchene and epi-β-santalene,[260] precapnelladiene,[261] damsin,[222,262] alpinigenine,[263] sarracenin,[227] and thienamycin.[264]

If the carbonyl group in fused rings is flanked by two methylene groups, the preferred regioisomer upon oxidation in the absence of overriding electronic considerations results from movement of the bond which best relieves steric strain in the Criegee intermediate. This usually results in migration of the group nearest the more highly substituted carbon.[265] Thus, A-nor-2-keto-steroids prefer migration of C-1 (70–100%) (Eq. 12).[266-268] Attack of peracid on the less-hindered α face of the car-



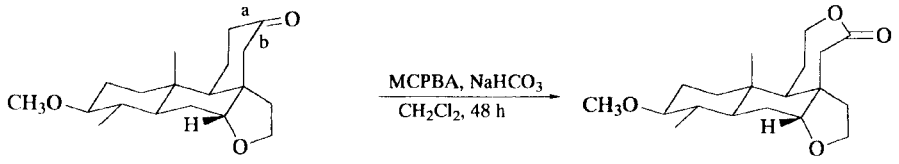
73 (80%) (20%)

(Eq. 12)

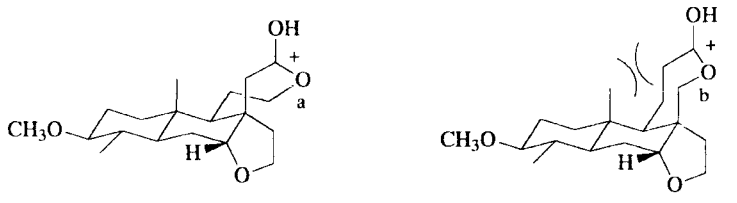
74

bonyl of **73** provides the Criegee intermediate **74**. Either C-1 or C-3 can orient *anti* to the peroxide bond, but there is greater relief of nonbonded interactions between the hydroxy and the bridgehead methyl when C-1 migrates.[267]

An exception in which the methylene group farthest from a tertiary bridgehead carbon migrates is the MCPBA oxidation of ketone **75** to give lactone **76**.[269,270] The adverse 1,3-diaxial steric interaction between the C-12 methylene and the axial C-10 methyl group encountered upon migration of bond **b** to give **77** is absent in **78**, formed by migration of bond **a**.

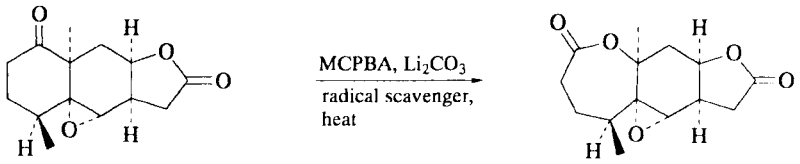


75 76 (66%)



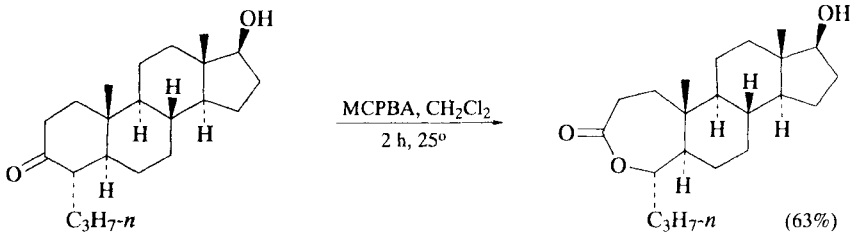
78 77

The Baeyer–Villiger cleavage of stereoselectively substituted fused six-membered rings, followed by lactone ring opening, results in a stereocontrolled route to side chains. Ring opening of lactone **79** is used in a synthesis of eriolangin and eriolanin;[223] other examples of this method include syntheses of glycinoeclepin A[271] and ivangulin.[272]



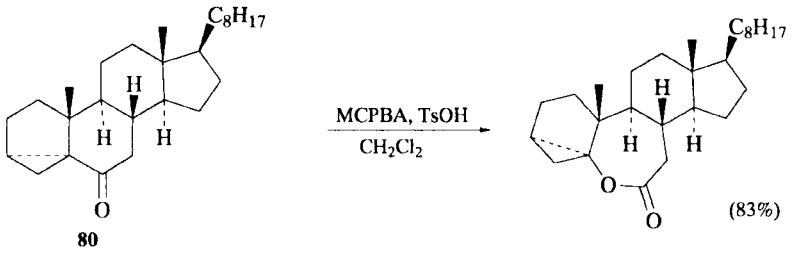
79 (81%)

The Baeyer–Villiger procedure has been applied to steroids with carbonyl groups at all possible ring positions. If there are no heteroatom substituents on the steroid or if the heteroatom substituent is far removed, then the major product of oxidation is derived from migration of the more substituted ligand. With carbonyl groups at C-1, C-4, C-6, C-7, C-11, C-12, C-13, and C-17 this results in preferential insertion of oxygen at a bridgehead position. Single regioisomers are reported except for some C-6[273] and C-17[274] ketones. Although single regioisomers are often reported, careful study of ketones flanked only by methylene groups indicates mixtures with insertion of oxygen mainly toward C-1 (75%) for 2-ketosteroids and primarily (90%) toward C-17 for 16-ketosteroids.[267,275] Although 3-ketosteroids show little regiochemical preference upon oxidation,[241,275] an *n*-propyl group at C-4 is sufficient to impart total regioselectivity (Eq. 13).[276]



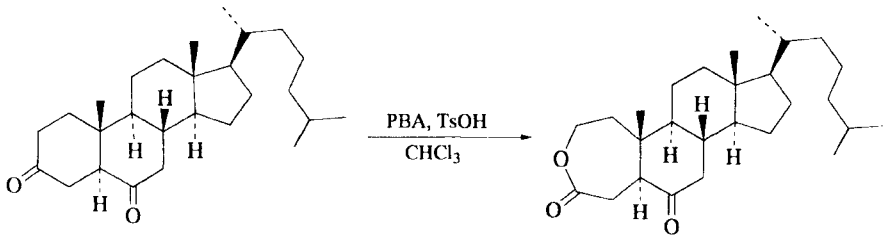
(Eq. 13)

The normal preference for oxidation of cyclopropyl ketones is primary > cyclopropyl.[42,45] However, the cyclocholestan-6-one **80** undergoes oxygen insertion next to the cyclopropyl group.[275,277]

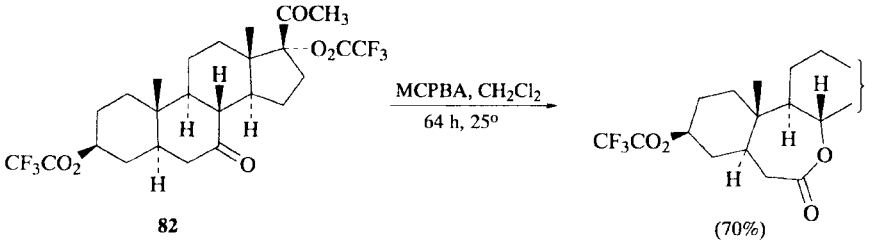


80

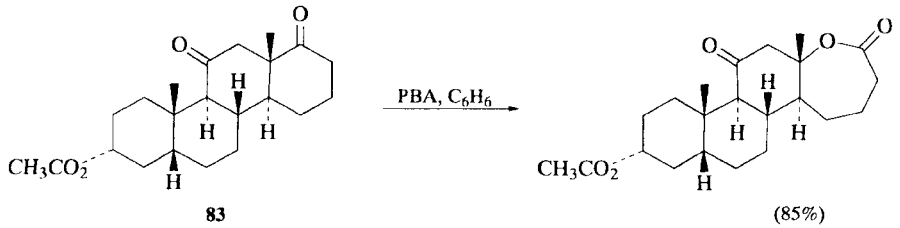
Cholestan-3-one has reactivity toward perbenzoic acid similar to that of cyclohexanone.[149] The rates of oxidation of steroidal ketones with perbenzoic acid show that a 3-ketosteroid reacts 30–80 times faster than a 17-ketosteroid, which reacts about twice as fast as a 20-ketosteroid.[149] Chemoselective oxidation of 5-α-cholestan-3,6-dione **81** introduces a single oxygen next to C-2.[278] The pregnan-7,20-dione **82**, a precursor of 7-oxaprogesterone, reacts only at the C-7 carbonyl,[279] and the D-homoetiocholan-11,17a-dione **83** reacts only at the C-17a.[280] A 3,17-diketo-



81 (63%)

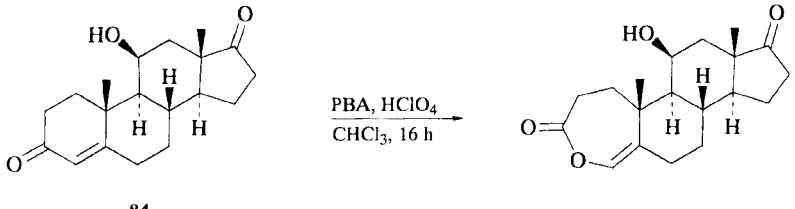


82 (70%)

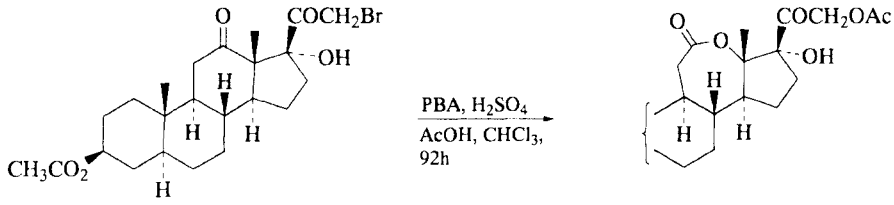


83 (85%)

4,5-dehydrosteroid **84** reacts only at C-3 with perbenzoic acid,[281] and a 12,20-diketosteroid **85** reacts only at C-12.[282,283]

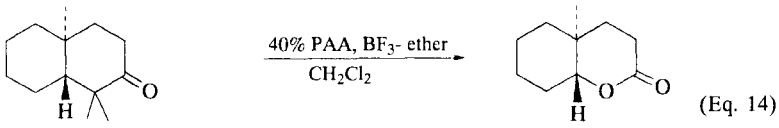


84 (60%)



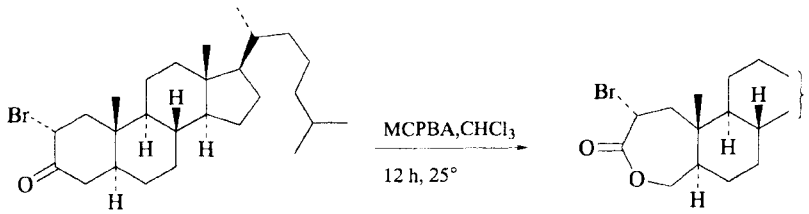
85 (36%)

When a 4,4-dimethyl substituted 3-ketosteroid, or similar fused system, is treated with peracetic acid in the presence of boron trifluoride an exhaustive oxidation occurs (Eq. 14).[284] The method is useful since the lactone formed can be used to make conjugated ketones.[251,284,285]



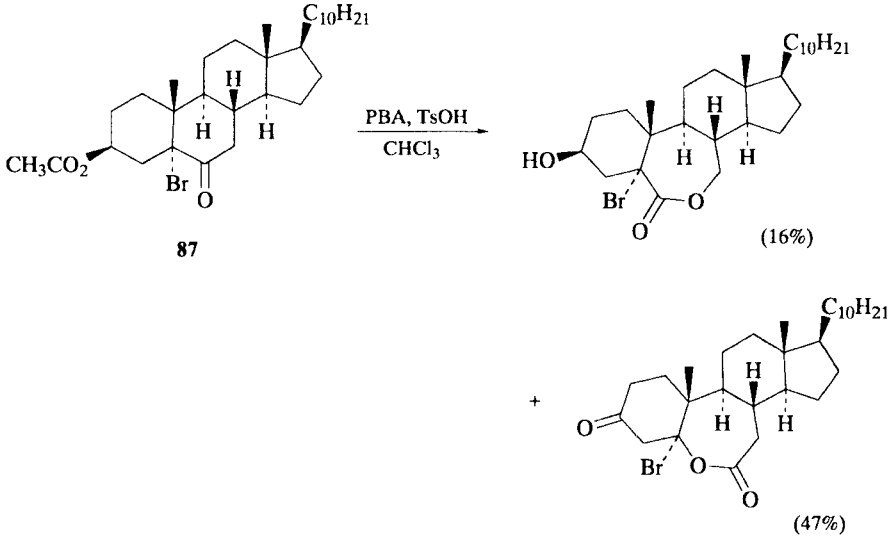
(41%) (Eq. 14)

Heteroatom substituents at the α position to the carbonyl have a marked effect upon the regiochemical outcome of Baeyer–Villiger oxidations of fused ring systems. An α-bromine atom usually retards migration of the attached carbon; this effect, as shown with bromoketone **86**, is the basis of a method for preparing regioisomerically pure lactones from 3-ketosteroids.[240,241,266,286] Insertion of oxygen



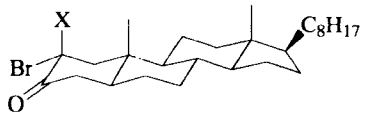
86 (97%)

adjacent to a bromine-containing bridgehead has been reported to **5-α-bromo**-cholestan-6-one[287] and the stigmastan-6-one **87**.[288]



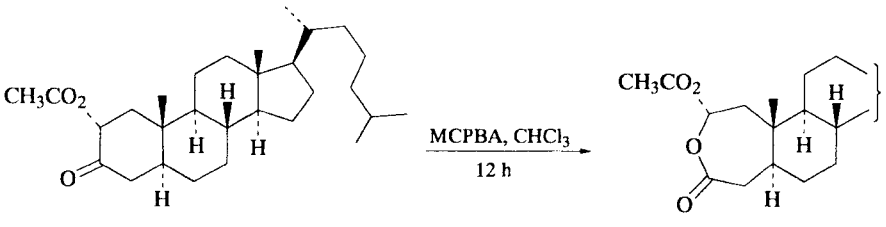
87

Relative to cholestan-3-one, α-2-bromocholestan-3-one (**88**) reacts 13 times slower and 2,2-dibromocholestan-3-one (**89**) reacts two times faster. The equatorial α bromine in the plane of the carbonyl decreases the polarity of the carbonyl bond and hinders reaction, while the axial β bromine facilitates reaction, since orbital interaction stabilizes a positive charge at the adjacent carbonyl.[149]



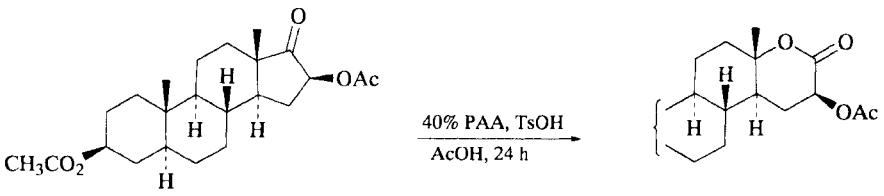
88 X = H
89 X = Br

An acetate ester α to the carbonyl in competition with a methylene group *generally* directs migration of the attached carbon,[289–291] as shown by the reaction of the 2-acetylcholestan-3-one (**90**).[199] An acetate-substituted carbon also migrates over a



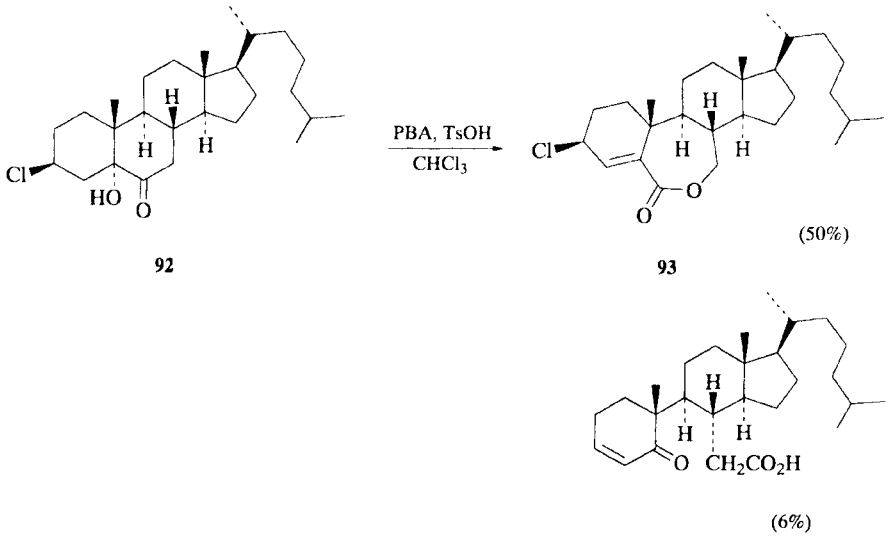
90

secondary bridgehead carbon.[292] A tertiary bridgehead carbon usually migrates in preference to a carbon attached to an acetoxy-substituted carbon as in the 16-acetoxyandrostanone **91**.[293,294]



91 (97%)

Migratory preferences with α hydroxy groups present are difficult to predict. A bridgehead 5-α-hydroxy group facilitates migration in a 3-acetoxy-6-ketosteroid,[295,296] but not in the oxidation of 3-chloro-5-α-hydroxycholestan-6-one (**92**), in which a methylene-migrated lactone **93** is the major isolated product.[288] Migration of a secondary carbon rather than a hydroxy-substituted carbon has been reported.[266]

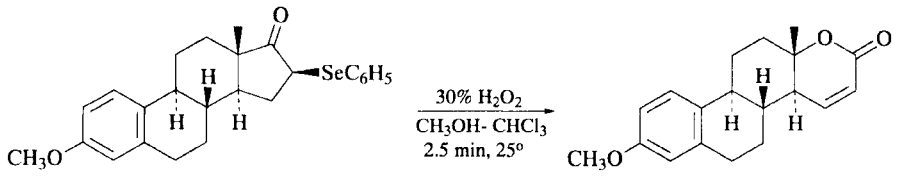


92 **93** (50%)

(6%)

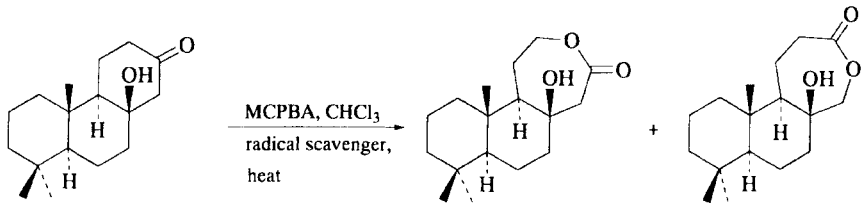
An α ether in the form of an epoxide normally facilitates migration;[297,298] however, when basic hydrogen peroxide is used as oxidant, C-1 migrates in a 2-keto-3,4-oxido-A-norsteroid.[299] Regioselective migrations occur when both adjacent methylenes have ether or ketal oxygen substituents; however, no clear pattern to predict migration has emerged.[300,301]

C-16-α-Phenylseleno ketones, such as **94**,[109] undergo rapid Baeyer–Villiger oxidation with regioselective bridgehead migration and selenoxide elimination when treated with 30% hydrogen peroxide. The active oxidizing agent is probably a peroxyseleninic acid generated in situ.[302]

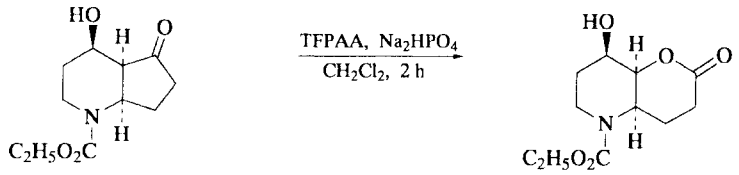


94 (66%)

A ketal oxygen at position C-5 of a 3-ketosteroid directs migration away from the proximal methylene,[303] but the β-hydroxy ketone **95** gives migration of both methylene groups.[304,305] The β-hydroxy and β-*N*-acyl substituents of ketone **96** do not block favored migration of the secondary bridgehead position.[85]

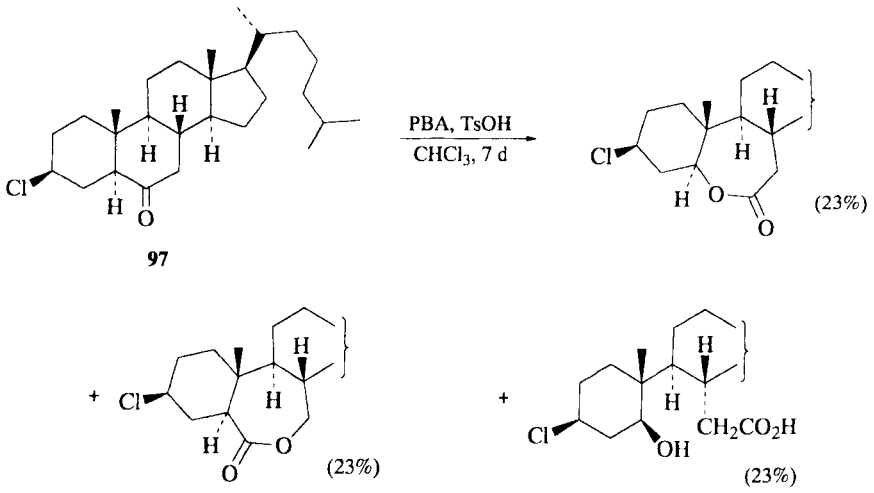


95 (34%) (49%)



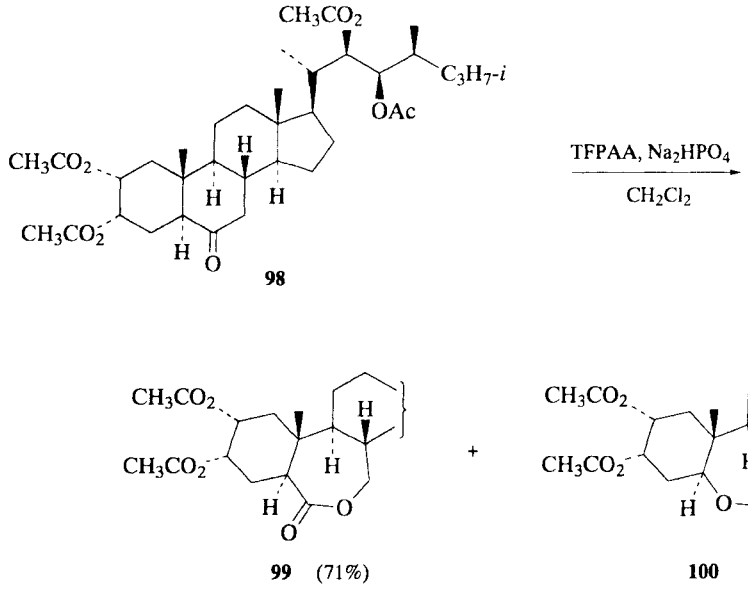
96 (50%)

The tendency for bridgehead migration in 6-ketosteroids is reduced by electron-withdrawing γ-halogen,[277,306–308] hydroxy,[306] or acetoxy[273,306,309,310] substituents at C-3.[287,303] The γ-chloroketone **97** affords a mixture of products from both bridgehead and methylene migration.[306] Electron withdrawal by 3-halo, 3-acyloxy, or 3-hydroxy substituents sometimes reduces the rate of MCPBA oxidation of 6-ketocholesterols. Relative to 6-ketocholesterol, a 3-α-chloro, 3-β-hydroxy, 3-β-acetate, or 3-β-bromo substituent cuts reaction rate in half while 3-β-chloro or 3-β-2,2-dimethylpropionate groups have neglible rate effects.[311]



97

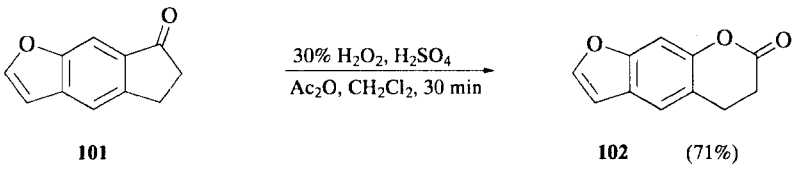
A systematic study of the effects of remote β, γ, and δ oxygen containing substituents on the regiochemistry of buffered TFPAA oxidations of 5-α-cholestan-6-one derivatives showed a minor percentage of migration of the C-5 bridgehead in all cases.[273] Since methylene migration dominates, the naturally occurring lactone brassinolide (**99**), a plant growth promoter, can be prepared from ketone **98**.[312,313] The regiochemistry of migration is catalyst dependent, since bridgehead migration to give lactone **100** is preferred if the oxidation of **98** is performed with TFPAA in methylene chloride with 1% sulfuric acid/10% acetic acid.[314]



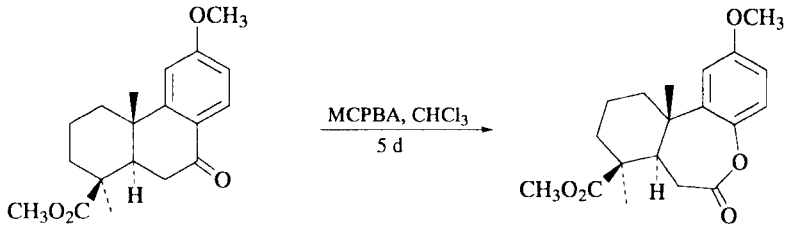
98

99 (71%) 100 (7%)

Oxidation of Benz-Fused Ketones. Psoralen (**102**) can be prepared from benz-fused ketone **101** by a regioselective migration of the aryl group over a primary methylene.[315] The Baeyer–Villiger procedure can be used to introduce an oxygen functionality at C-11 of structures similar to ketone **103** by ring opening of the derived lactone **104**, rotation, and Friedel–Crafts acylation at the original C-11.[116]

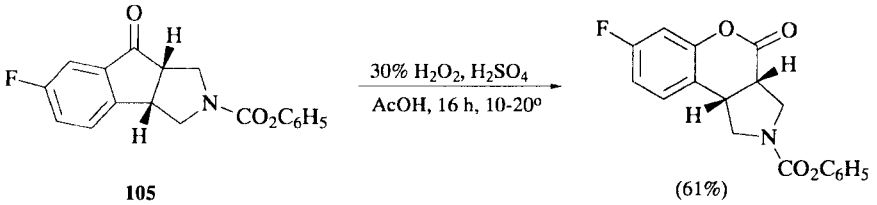


101 **102** (71%)



103 **104** (88%)

Preferential migration of an aryl ring is also generally preferred over a secondary carbon. Aryl migration is aided by an electron-donating *o*- or *p*-acetate on the ring.[316] The ring fluorine does not deter aryl migration in ketone **105**, in which alkyl migration may be deterred by the β-carbamate substituent.[317] An example of preferential secondary-alkyl migration is reported, but in extremely low yield.[318] If a ketone is di-benz-fused, the preferential migrating group is the more electron-releasing one.[2,319,320]



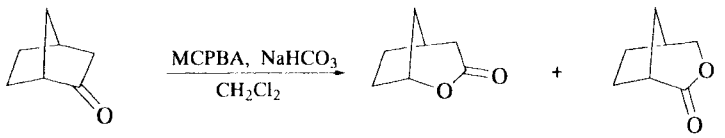
105 (61%)

Reactions of Bridged Bicyclic and Polycyclic Ketones

The ketones in this section, irrespective of unsaturation or heteroatom substitution, are organized according to the structure of the parent bridged hydrocarbon. For polycyclic ketones, the ring system is considered to be the bridged bicyclanone with

the smallest sum for the three bridging units, and the ring system is numbered arbitrarily as this bicyclic ketone would be numbered.

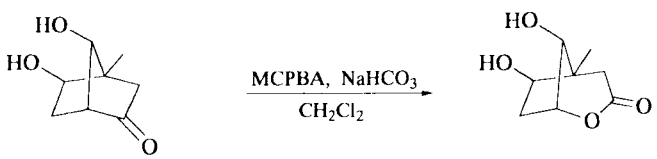
Oxidation of Bicyclo[2.2.1]heptanones. Baeyer–Villiger oxidation of norbornan-2-one (**106**), which is available in chiral form,[321] provides mainly the bridgehead migrated lactone **107**.[322,323] This lactone serves as a rigid template for further functionalization reactions, and is used in stereocontrolled syntheses of the cinchona,[324,325] yohimbane,[325] emetine,[326,327] and coryanthe-type alkaloids.[328]



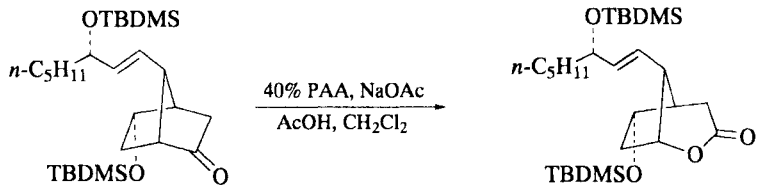
106 **107** (79%) (7%)

Substituted norbornan-2-ones provide access to polyfunctional cyclopentanol derivatives; lactone **108** is an intermediate in the synthesis of verrucarol.[329–331] Oxidation of the prostaglandin precursor **109** provides a mixture of regioisomeric lactones **110** and **111**.[332,333] The minor methylene-migrated lactone **111** can be removed by preferential hydrolysis with dilute aqueous base.[334,335] In addition to extensive use in prostaglandin syntheses,[332,333,336–353] substituted norbornan-2-ones are precursors of (–)-terrecyclic acid **A**,[354] boschniolactone,[355] triquinacine,[334] a 19-norsteroid,[356] spatane diterpenes,[357] and methyl dihydrojasmonate.[358,359]

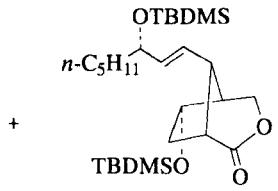
The preference for bridgehead migration in the oxidation of norbornan-7-ones can be altered by substitution at C-3 and C-7.[9] A single methyl group at C-3 results in a 1:1 mixture of bridgehead and nonbridgehead migrated lactones;[360] the formation of mainly lactone **114** from fenchone (**112**) has been attributed to greater relief of eclipsing interactions in the Criegee intermediate **113** for movement of C-3.[361,362]



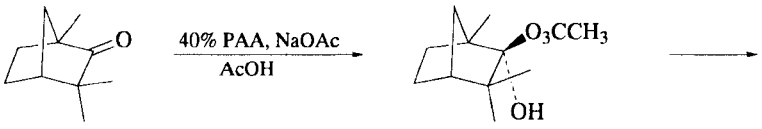
108 (95%)



109 **110** (79%)



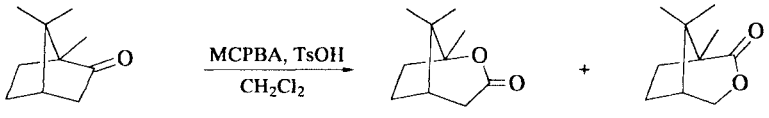
111 (21%)



112 **113**

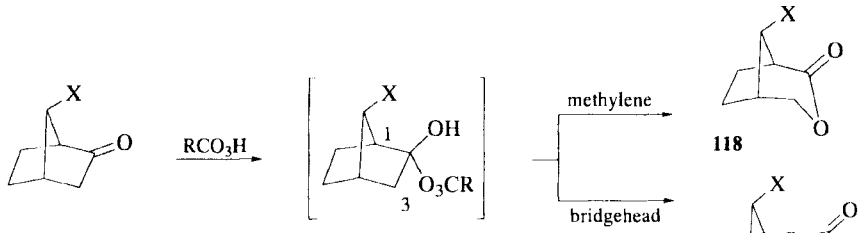
114 (21%) (14%)

Bridgehead migration is favored upon oxidation of 1-methylbicyclo[2.2.1]heptan-2-one.[323,362] Oxidation of camphor (**115**) also gives preferred C-1 migration.[362–364] However, in those cases where stereochemistry has been unambiguously defined[365] and the bridgehead C-1 is unsubstituted,[362,363,366] oxidation of a 7-*syn*-methyl-,[362,367,368] 7-*syn*-halogen-,[361,369] or 7-*syn*-methoxy-substituted norbornan-2-one (**116**)[369] results in preferential methylene migration. An argument that has been



115 (47%) (31%)

advanced to explain this phenomenon assumes that the 7-*syn* substituent blocks attack of the peracid from the *exo* direction and gives rise to the Criegee intermediate **117**. Migration of the C-3 methylene carbon involves a lower energy transition state proceeding through a chair-like conformation to give **118**, while migration of the C-1 bridgehead carbon proceeds through a less favored boat-like conformation to **119**.[361,362,370,371] In support of this suggestion, if a 7-*syn* substituent facilitates addition of peracid to the *exo* face by hydrogen bonding or other interaction,[358] bridgehead migration is preferred. Accordingly, with MCPBA and a 7-*syn*-carboxylic acid (100%),[371a] 7-*syn*-methoxycarbonyl (95%),[358,369] 7-*syn*-hydroxymethyl (100%),[371b] 7-*syn*-acetate (60%),[369] or 7-*syn*-*p*-toluenesulfonyl[369] (62%) group, bridgehead migration dominates.



116 X = CH_3, Br, Cl, OCH_3

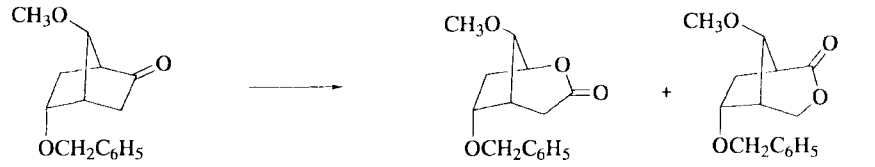
117

118

119

Norbornan-2-ones with *tert*-amino,[347,371c] acetate,[369] methoxy,[369] or carbomethoxy[369] substituents in the 7-*anti* position, which is beta to the migrating bridgehead and sterically remote from the C-2 carbonyl, undergo bridgehead migration during oxidation. As the electron-withdrawing power of the 7-*anti* substituent increases,[371c] the propensity for bridgehead migration decreases; for example, 7-*anti*-cyano (0% bridgehead)[349] and 7-*anti*-*p*-toluenesulfonyl (60% bridgehead).[369] A second substituent at C-5-*endo* also has an influence on the regiochemical outcome.[371c] Oxidation of 5-*endo*-acetoxy-7-*anti*-methoxynorbornan-2-one with performic acid gives 70% bridgehead:30% methylene migration.[349]

The choice of peracid and solvent influences regiochemistry in the oxidation of 5-*endo*-benzyloxy-7-*anti*-methoxynorbornan-2-one (**120**) (Table 4).[349] The selectivity for bridgehead migration is greatest with peracetic acid in the weakly acidic acetic acid solvent. Preference for migration of the more electron-donating bridgehead carbon, which can better stabilize the transition state for loss of acetic acid during



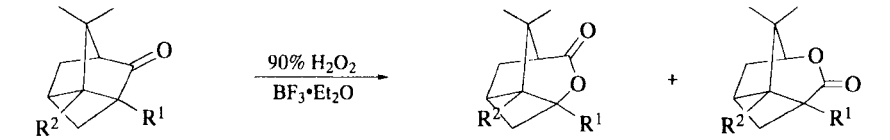
120 **121** **122**

TABLE 4. THE EFFECT OF PERACID ON THE REGIOSELECTIVITY OF THE BAEYER–VILLIGER REACTION OF NORBORNAN-2-ONE **120**[349]

Peracid	Solvent	Ratio (**121**:**122**)
MCPBA	CH_2Cl_2	55:45
Permaleic	CH_2Cl_2	67:33
Perphthalic	$CHCl_3$	73:27
Performic	HCO_2H	85:15
Peracetic	CH_3CO_2H	92:8

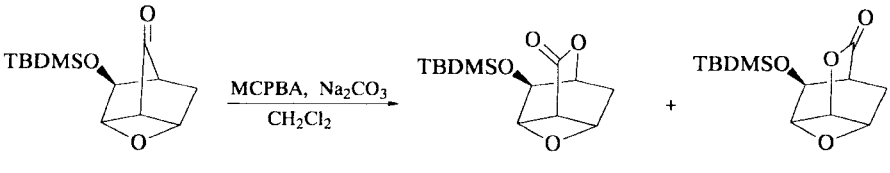
decomposition of the reactive Criegee intermediate, assumes greater importance with a poor leaving group.

The 2-methyl-2,6-methylene-bridged norbornan-2-one **123** inserts oxygen only at the tertiary cyclobutyl carbon to give lactone **124**; an unspecified mixture of regioisomers forms from **125** when the methyl is not adjacent to the carbonyl.[372] The bridged norbornan-7-one **126** undergoes regioselective oxidation to lactone **127**.[373] The electronegative oxetane retards migration. If the 2,6 position of a 7-norbornanone is bridged by a methylene instead of an oxygen, only migration of the cyclobutyl ring occurs.[374] Migration of a secondary bridgehead carbon is preferred over a bridgehead cyclopropyl carbon in the oxidation of the bridged norbornan-2-ones **128**.[340,343,375,376]

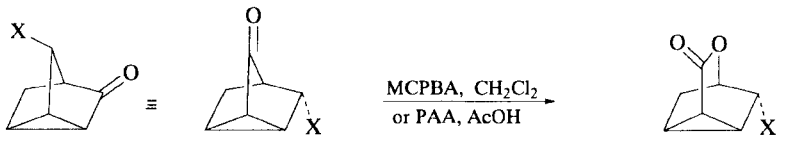


123 $R^1 = CH_3$, $R^2 = H$ ⟶ (76%) **124**

125 $R^1 = H$, $R^2 = CH_3$ ⟶ (56%) mixture of both lactones

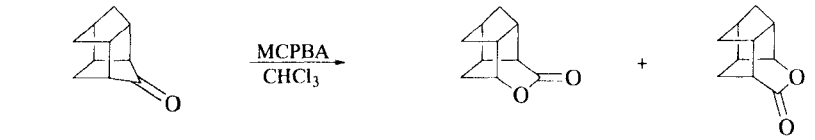


126 **127** (83%) (9%)

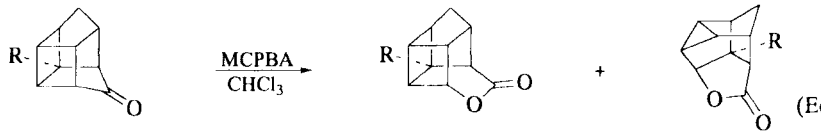


128 X = H, CO_2CH_3, CO_2H (56-100%)

The caged structures **129** and 1,4-bis-homocubanone (**130**) are formally bicyclo[2.2.1]heptan-7-one derivatives.[377,378] Oxidations of related bis-homocubanones with peracetic acid or MCPBA generally insert oxygen preferentially toward the cyclobutane ring,[377-380] although regioisomeric mixtures are reported.[378] Oxidations of caged ketones are often accompanied by rearrangement (Eq. 15).[377,379] Conversion of the caged structure homopentaprismanone to pentaprismane involves a Baeyer–Villiger oxidation.[381]



129 (67%) (21%)

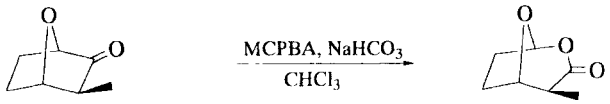


(Eq. 15)

130
R = $CO_2CH_2C_6H_4NO_2$-*p*

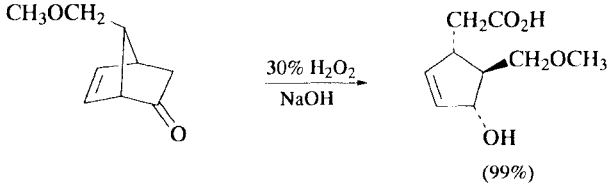
(54%) (16%)

The α-oxygen atom of 7-oxanorbornan-2-one (**131**), in competition with a secondary carbon, directs migration toward the bridgehead.[382-386] Lactone **132** is a precursor of methyl nonactate,[382,383] and lactones derived by oxidation of 5,6-substituted-7-oxanorbornanones are used to prepare carbohydrates[382,385-388] and alkaloids.[388a-e]



131 **132** (94%)

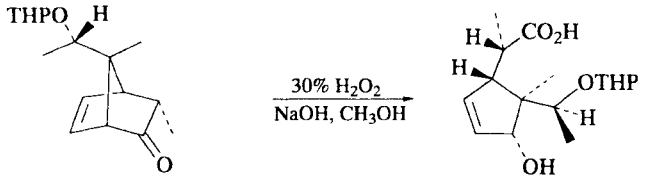
The lactone formed upon oxidation of norbornen-2-one has been used to prepare the cyclopentane ring of brefeldin-A,[389] and substituted norbornen-2-ones have found extensive use in the synthesis of prostaglandins[337,344,390-411] and prostacyclins.[412] Chemospecific oxidations with regiospecific bridgehead migration occur with basic 30% hydrogen peroxide (Eq. 16).[390] The preference for migration of the



(Eq. 16)

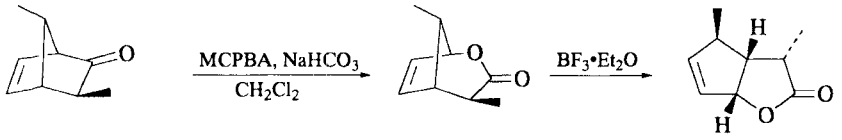
(99%)

allylic bridgehead is unaffected by substitution of a 7-*syn* methyl group[60,262,405,413-415] or by 3-methyl groups.[60,405,414-416] The hydroxyacid **134** formed upon oxidation of ketone **133** has been utilized in the synthesis of pseudoguaianolides,[405,414,415] and similar structures modified at C-7-*anti* and C-3 have been utilized to prepare a helenanolide[405] and estrone.[413]



133 **134** (75%)

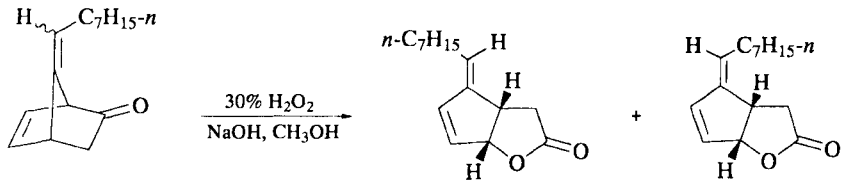
If the lactone or hydroxy acid derived from a norbornen-2-one is treated with a Lewis acid in an aprotic solvent, an isomeric fused-ring lactone derived by allylic alcohol rearrangement is formed (Eq. 17).[417] This rearrangement has been used to



135 (84%)

(Eq. 17)

synthesize lactone **135**, a precursor of the Prelog–Djerassi lactone,[416] and to prepare lactones used in the synthesis of a sterol D-ring and side chain,[413,414] thienamycin,[418] and the Inhoffen-Lythgoe diol.[60] Oxidation of 7-alkenylnorbornenones gives only epoxidation with MCPBA, but provides allylically rearranged lactones with basic hydrogen peroxide (Eq. 18).[409]

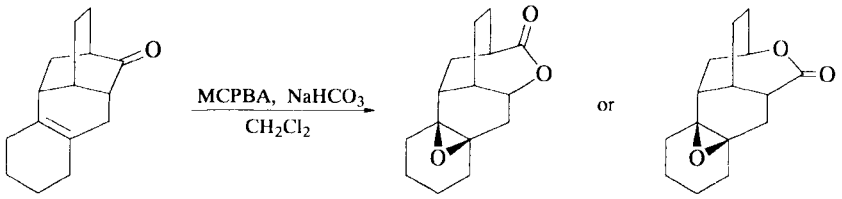


(42%) (21%)

(Eq. 18)

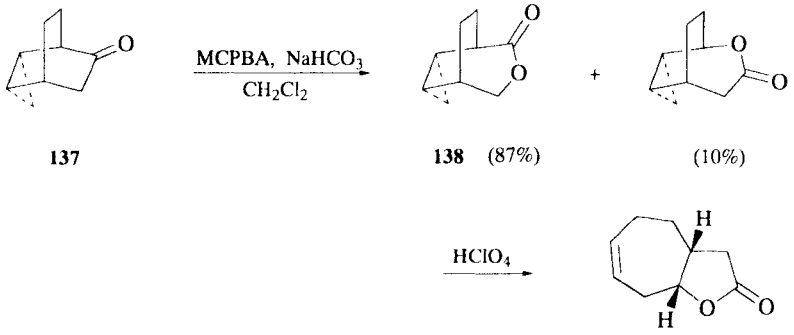
Oxidation of Bicyclo[2.2.2]octanones. Baeyer–Villiger oxidation of bicyclo-[2.2.2]octan-2-ones unsubstituted on the C-3 methylene carbon gives solely

bridgehead migration.[371,419,420] MCPBA oxidation of ketone **136**, which has two secondary alkyl substituents, nevertheless provides a single unidentified lactone regioisomer.[421] Unlike the *syn*-cyclopropyl isomer in the norbornan-2-one series,

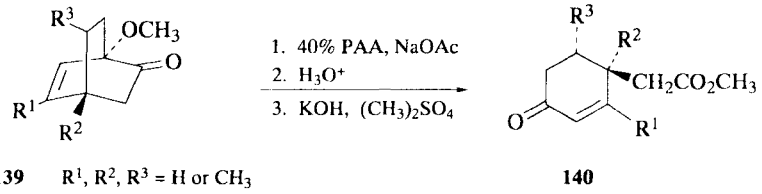


136

which has an 80:20 preference for bridgehead migration, oxidation of the *syn*-cyclopropyl ketone **137** results in major methylene migration to give **138**. The *anti*-cyclopropyl isomer of **137** and *anti*-cyclopropyl homolog in the norbornan-2-one series give only bridgehead migration.[422] Oxidation of 1-methoxybicyclo[2.2.2]octenones **139** with bridgehead migration and lactone ring opening provides 4,4-disubstituted cyclohexenones **140**.[423]



137 **138** (87%) (10%)



139 R^1, R^2, R^3 = H or CH_3 **140**

The bridgehead nitrogen atom facilitates cleavage of 1-azabicyclo[2.2.2]octan-3-one (**141**) between the carbonyl and adjacent methylene group.[73] The effect of substituent and peracid upon the regiochemistry of migration of 3-substituted 2-azabicyclo[2.2.2]octan-5-ones **142** is shown in Table 5.[424-426] Peracetic acid is more regioselective for bridgehead migrated lactones **143** than is MCPBA. Peracetic

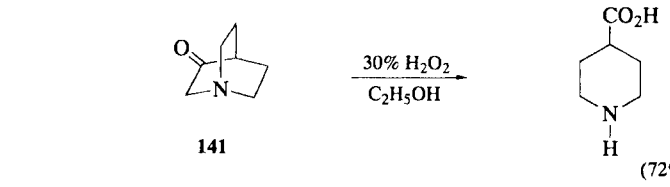
TABLE 5. EFFECTS OF 3-SUBSTITUENTS ON THE REGIOCHEMISTRY OF OXYGEN INSERTION OF *N*-CARBOBENZOXY-2-AZABICYCLO[2.2.2]OCTAN-5-ONES **142**[424]

R	R^1	Peracid[a]	BH Migration (% of **143**)[b]	Yield (%)
H	H	PAA	100	90
		TFPAA	100	61
		MCPBA	69	89
		PNPBA[c]	67	78
H	CH_3	PAA	62	71
		MCPBA	50	85
H	C_6H_5	PAA	100	74
		MCPBA	60	83
H	$CH_2O_2CC_6H_5$	PAA	84	16
H	CO_2CH_3	PAA	100	60
		MCPBA	18	70
CH_3	H	PAA		0
		MCPBA	81	71
CO_2CH_3	H	PAA	66	57
		MCPBA	38	91

[a]PAA = 40% PAA/AcOH, NaOAc; MCPBA and PNPBA in CH_2Cl_2, $NaHCO_3$; TFPAA = 89% TFPAA, Na_2HPO_4, CH_2Cl_2.

[b]BH = bridgehead migrated lactone.

[c]PNPBA = *p*-nitroperbenzoic acid.



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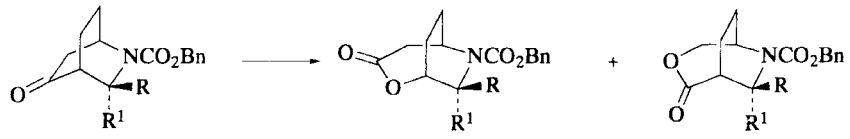
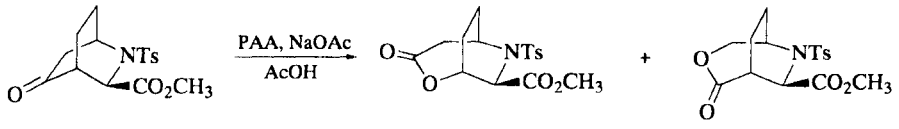


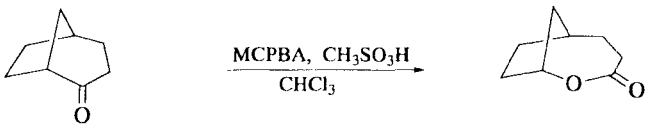
142 **143**

acid oxidation of *N*-tosyl ketone **144** provides lactone **145**, a precursor of isoprosopinine B.[427]



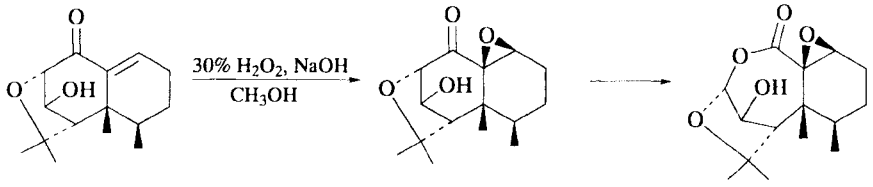
144 **145**

Oxidation of Bicyclo[3.2.1]octanones. Oxidation of bicyclo[3.2.1]octan-2-ones with PAA[428,429] or MCPBA gives mainly bridgehead migration;[430] lactone **146**

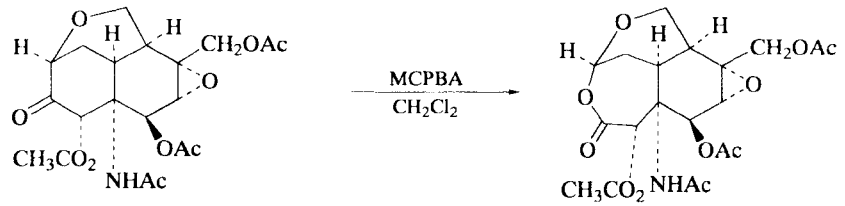


146 (80-90%)

was utilized in the synthesis of peristylane.[431] Regioselective bridgehead oxygen insertion is observed upon oxidation of 8-oxabicyclo[3.2.1]octan-2-ones, which have a ketal oxygen at C-3.[301] An α-ether oxygen adjacent to the bridgehead directs exclusive bridgehead migration for 7-oxabicyclo[3.2.1]octan-2-ones **147** and **148** in competition with 3-alkenyl (3-α-epoxide) or 3-acetoxy substituents.[432,433]

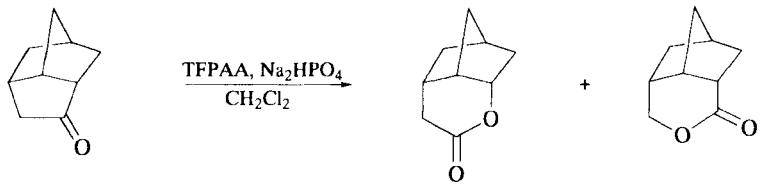


147 (43%) (—)



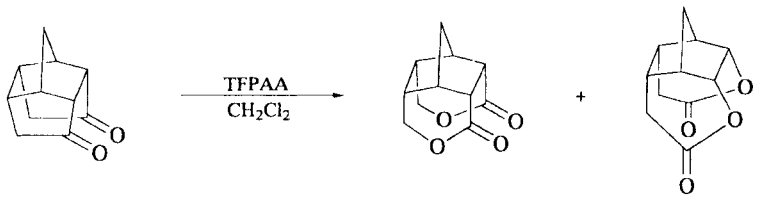
148 (100%)

Bicyclo[3.2.1]octan-6-ones normally oxidize with regioselective bridgehead migration.[434-436] However, oxidation of brendanone (**149**), a bridged bicyclo[3.2.1]-octan-6-one, provides a mixture of lactones with TFPAA,[437] and the tetracyclic

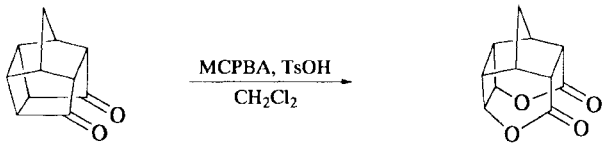


149 (46%) (38%)

ketone **150** gives nearly totally dimethylene migrated lactone **151**.[438] The related pentacyclic ketone **152** prefers cyclobutyl–carbon migration.[439,440] Major migration occurs away from the bridgehead if a C-7-α-methyl is introduced onto a bicy-

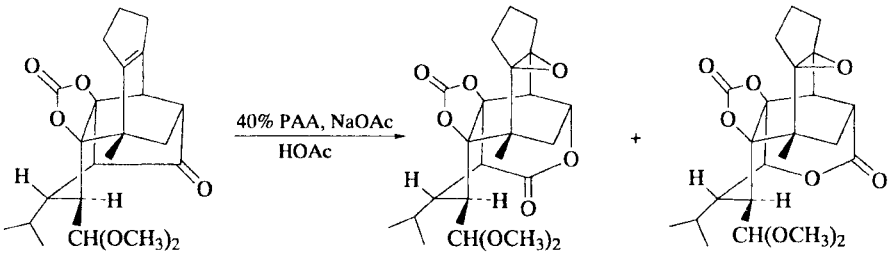


150 **151** (>71%) (<4%)



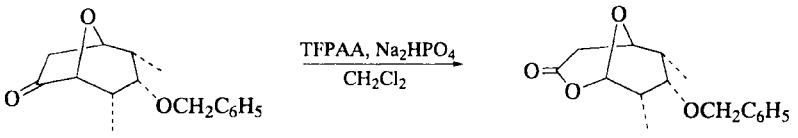
152 (81%)

clo[3.2.1]octan-6-one;[436] however, the polycyclic ketone **153** provides mainly the epoxylactone **154**, an intermediate in a synthesis of ryanodol.[441]



153 **154** (69%) (12%)

Bridgehead migration is favored by an oxygen atom adjacent to the bridgehead, and 8-oxabicyclo[3.2.1]octan-6-ones undergo regioselective bridgehead insertion of oxygen (Eq. 19).[442] Lactone **155** was used to prepare the C_{21}–C_{27} segment of rifamycin S.[443]

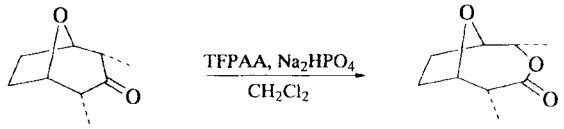


155 (80%)

(Eq. 19)

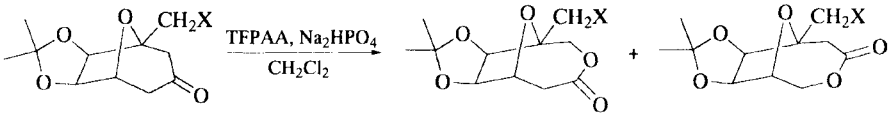
Oxidation of bicyclo[3.2.1]octan-3-one with MCPBA (56 hours, 25°) is slow,[444,445] and bicyclo[3.2.1]octa-3,8-dione (**156**) reacts only at C-8 with MCPBA.[444] Oxidation of an 8-*N*-methoxycarbonyl analog with MCPBA is successful under forcing conditions after 22 hours at 55° in the presence of the radical inhibitor 2,4,6-tri(*tert*-butyl)phenol.[446] The 3-carbonyl group of 8-oxabicyclo-[3.2.1]octan-3-ones is oxidized without difficulty (Eq. 20). Lactone **157** is converted to nonactic acid.[447]

156 (86%) (Eq. 20)

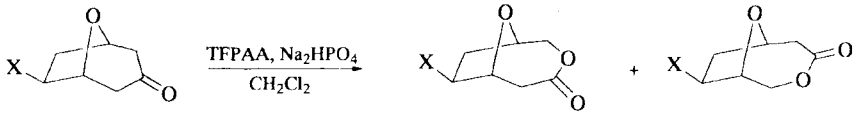


157 (94%)

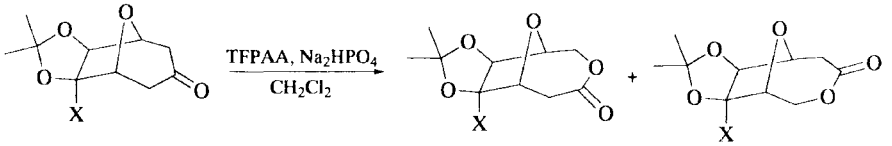
The Baeyer–Villiger oxidation of 8-oxabicyclo[3.2.1]octan-3-ones is used in the synthesis of *C*-nucleosides.[38,448-463] The electronic effects exerted by remote γ substituents upon the regiochemistry of oxidations of ketones **158** and **159** is shown in Table 6. An increase in electron-withdrawing ability of the γ group X



158



159

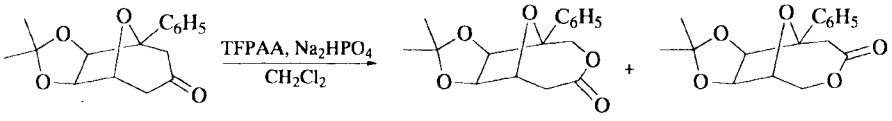


160

TABLE 6. EFFECTS OF γ SUBSTITUENTS ON THE REGIOSELECTIVITY OF OXIDATION WITH 8-OXABICYCLO[3.2.1]NONAN-3-ONES **158–160** WITH TFPAA[9,38]

Ketone (X Position)	γ-Substituent X	α-migration (%)
158 C-1′	$OSi(CH_3)_2C_4H_9$-*t*	55
	H	53
	C_4H_9-*n*	50
	$OCH_2C_6H_5$	48
	O_2CCH_3	35
	$O_2CC_4H_9$-*t*	31
	$O_2CC_6H_5$	28
	O_2CCF_3	23
	OSO_2CH_3	19
	OSO_2CF_3	14
159 C-6-*exo*	$OSi(CH_3)_2C_4H_9$-*t*	30
	$OCH_2C_6H_5$	30
	O_2CCH_3	46
	$O_2CC_4H_9$-*t*	35
	$O_2CC_6H_5$	35
160 C-6-*endo*	CH_3	33
	C_5H_{11}-*n*	25
	C_4H_9-*t*	—
	C_6H_5	39
	$CH_2OCH_2C_6H_5$	23
	$CH_2O_2CC_6H_5$	40
	$CH_2OSi(CH_3)_2C_4H_9$-*t*	26
	$CH_2O_2CC_4H_9$-*t*	34

results in a decreased tendency of the nearest α carbon to migrate to an electron-deficient center of a Criegee intermediate.[9,38,39] With a C-1 phenyl group oxidation is highly regioselective for migration of the α-methylene group (Eq. 21).[38]

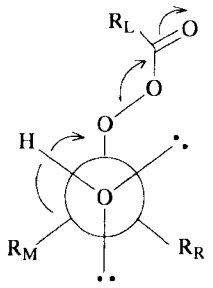


(82%) (11%)

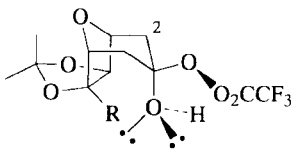
(Eq. 21)

Steric effects on the regioselectivity of oxygen insertion of 6-*endo*-substituted-8-oxabicyclo[3.2.1]octan-3-ones **160** are shown in Table 6.[9,38,40] Conversions are below 50% with TFPAA after 36 hours at 25° in methylene chloride because of the low equilibrium concentrations of tetrahedral Criegee intermediates; a *tert*-butyl group blocks oxidation. The bulky substituent decreases the tendency for the nearest methylene carbon to migrate. This finding contrasts with the tendency in steroidal A-ring ketones for the more sterically hindered methylene to migrate preferentially, but can be explained.[267] In order for a group R_M in a tetrahedral Criegee intermedi-

ate to migrate to oxygen with ejection of carboxylic acid two prerequisites must be met. The groups R_M-C-O-O of **6** should have R_M and the distal oxygen in an antiperiplanar geometry. Additionally, one of the hydroxy nonbonding electron pairs must also be antiperiplanar to R_M. These requirements are met by conformation **7**, from which the C-2 carbon farthest from the group R can migrate. The conformation which results in migration of C-4 is disfavored by nonbonded repulsion of the group R and the hydroxy hydrogen, which must now be on the same side of the molecule as R.[9,38,40]

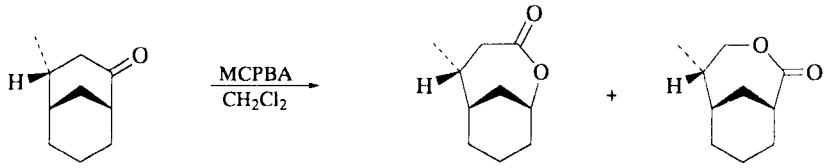


6



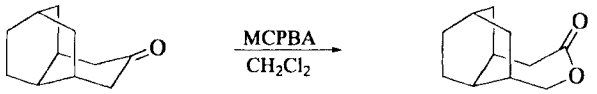
7

Oxidation of Bicyclo[3.3.1]nonanones. Bicyclo[3.3.1]nonan-2-one oxidizes with MCPBA[444] or TFPAA to give a bridgehead migrated lactone.[464] Oxidation of ketone **161** with peracetic acid gives mainly lactone **162**, an intermediate in the synthesis of *erythro*-juvabione.[465]

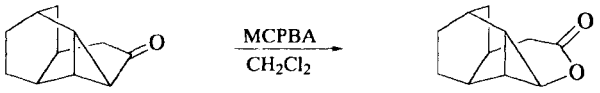


161 **162** (81%) (14%)

MCPBA does not oxidize bicyclo[3.3.1]nonan-3-one,[444] and the olefin of an internal C-6 double bond or a 7-*exo*-methylene on a bicyclo[3.3.1]nonan-3-one is more reactive than the C-3 carbonyl.[466–468] Bicyclo[3.3.1]nonan-3,9-dione reacts only at the 9 position.[444] Failure of the 3-keto group in such systems to undergo Baeyer–Villiger oxidation is attributed to steric hindrance toward formation of the tetrahedral Criegee intermediate. In agreement with this reasoning, bicyclo[3.3.1]-nonan-3,7-dione[466,469] and 7-*exo*-dicyanomethylenebicyclo[3.3.1]nonan-3-one,[466] in which the olefin is deactivated toward electrophilic addition, are oxidized by MCPBA to lactones. Also, when the 7-*endo*-methylene hydrogen is tied back as in ketones **163** and **164**, MCPBA affords lactones.[444] Regioselective cyclopropyl migration to give **165** differs from the reactivity order of primary > cyclopropyl ob-

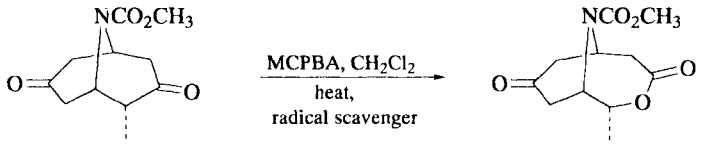


163 (86%)



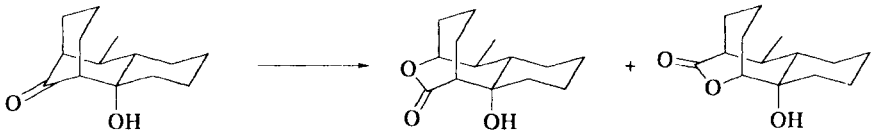
164 **165** (88%)

served in oxidations of open-chain ketones.[42,45] Chemoselective and regioselective oxidation of the 9-azabicyclo[3.3.1]nonan-3-one **166** provides the palustrine intermediate **167**.[470]



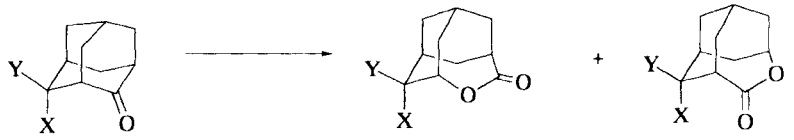
166 **167** (93%)

Bicyclo[3.3.1]nonan-9-ones oxidize with 40% peracetic acid,[471] monoperphthalic acid,[472] TFPAA,[473] or perseleninic acid.[474] A β-hydroxy group in **168** retards migra-



168 (36%) (24%)

tion of the α bridgehead.[475] Only migration of the distal bond to give lactones **171** is observed during PAA and MCPBA Baeyer–Villiger oxidations of *syn*-X and *anti*-Y 4-substituted adamantanones **169** with strongly electron-withdrawing methoxy, acetoxy, methanesulfonyl, and cyano substituents (Eq. 22). As shown by the per-

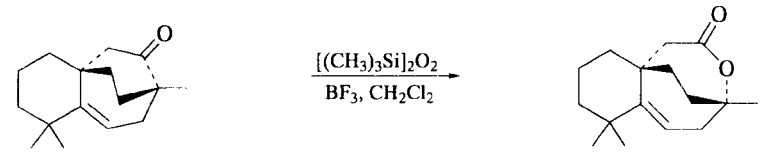


169 **170** **171**

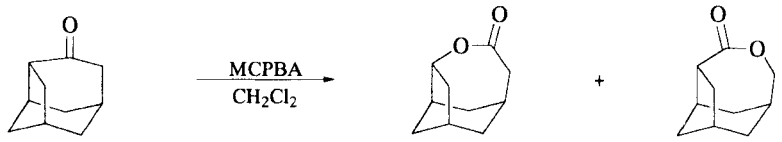
X or Y = OCH_3, O_2CCH_3, OSO_2CH_3, CN, Cl, Br, I, C_6H_5, H and H (Eq. 22)

centages in parentheses, less electron-withdrawing *anti*-Y/*syn*-X chloro (6%/7%), bromo (5%/20%), and phenyl (33%/50%) substituents afford increasing amounts of proximal bond migration product **170**. There is a moderate sensitivity to substituent stereochemistry. Iodo (71%/55%) adamantanones **169** give major lactone **170**, but hydrogen peroxide/selenium dioxide is used as the oxidant. The *syn* epimers are generally less reactive.[476]

Oxidation of Bicyclo[3.2.2]nonanones. In a synthesis of widiol, the bicyclo[3.2.2]nonan-6-one derivative **172** is oxidized chemoselectively with *bis*-trimethylsilyl peroxide.[477] Bridgehead migration is preferred with MCPBA oxidation of 4-protoadamantanone **173**, a methylene-bridged bicyclo[3.2.2]nonan-6-one.[478]



172 (43%)



173 (60%) (40%)

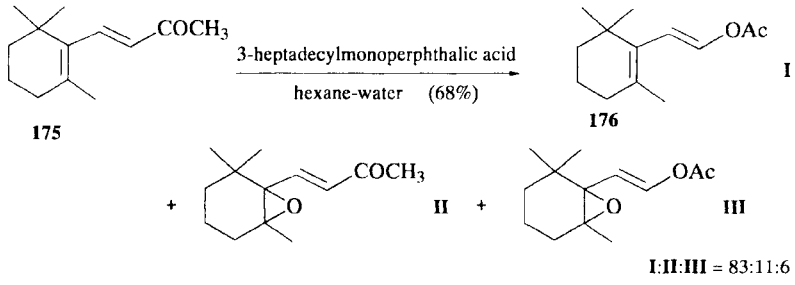
Oxidation of Bicyclo[4.3.1]decanones. Bicyclo[4.3.1]decan-8-one retains sufficient conformational flexibility that Baeyer–Villiger oxidation succeeds after 240 hours with MCPBA.[444] Bicyclo[4.3.1]decane-8,10-dione reacts only at the C-10 carbonyl with MCPBA after 24 hours.[444] The tricyclic diketone **174** reacts regioselectively and chemoselectively with MCPBA solely at the less-hindered carbonyl.[479]

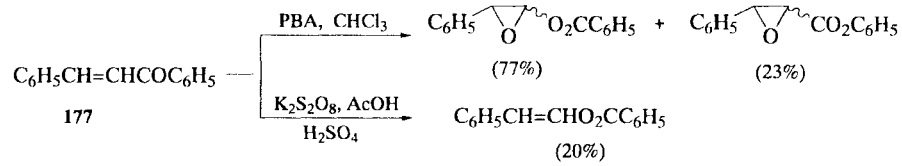
174 (60%)

Reactions of α,β-Unsaturated Ketones

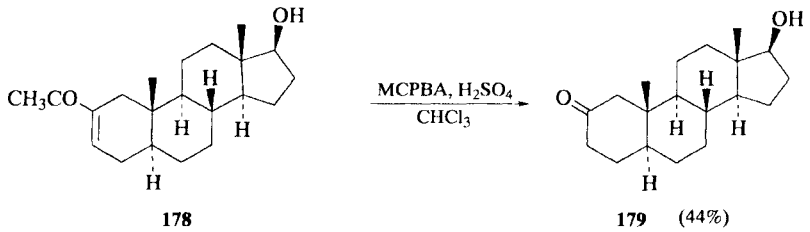
Oxidation of Acyclic Conjugated Ketones. Epoxidation of acyclic methyl vinyl ketones is often favored over Baeyer–Villiger oxidation.[2,480–482] Although epox-

idation of the endocyclic double bond of β-ionone **175** cannot be avoided using MCPBA or perbenzoic acid,[483,484] the monosodium salt of 3-heptadecylmonoperphthalic acid in a hexane–water emulsion system gives mainly the enol ester **176**.[484] Oxidation of phenyl vinyl ketone **177** is only partially regioselective and is accompanied by olefin epoxidation;[485] however, persulfuric acid affords a small yield of enol ester.[486]





Oxidation of Monocyclic Conjugated Ketones. Monocyclic conjugated ketones are of three types depending upon whether the olefin and carbonyl groups are endocyclic or exocyclic to the ring. Cyclohexenyl methyl ketones, which have an endocyclic olefin and an exocyclic carbonyl, give primarily enol acetates and minor amounts of epoxy acetates with MCPBA.[487,488] As part of a 1,2-ketone transposition method which begins with a 3-ketosteroid, cyclohexenyl ketone **178** is oxidized to



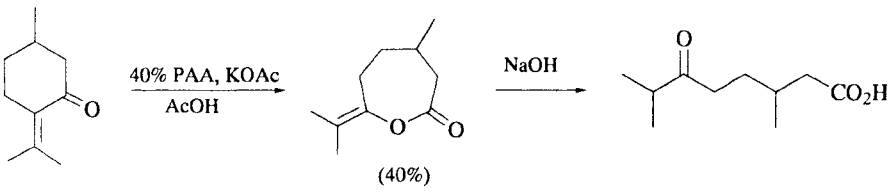
178 **179** (44%)

an intermediate enol acetate, which hydrolyzes to 2-ketosteroid **179**.[488] Cyclopentenyl ketone **180** affords only epoxyacetate with MCPBA;[488] however, the fused-ring ketone **181** yields an enol acetate.[489]

180 (35%)

181 (—)

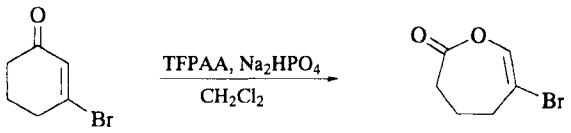
Peracetic acid or MCPBA convert *exo*-alkenylcycloalkanones mainly to enol lactones,[106,490,491] although minor amounts of epoxy ketone can be formed (Eq. 23).[106] Keto acids usually are isolated from reactions of *exo*-alkylidenecyclopentanones with basic hydrogen peroxide.[158,179]



(40%)

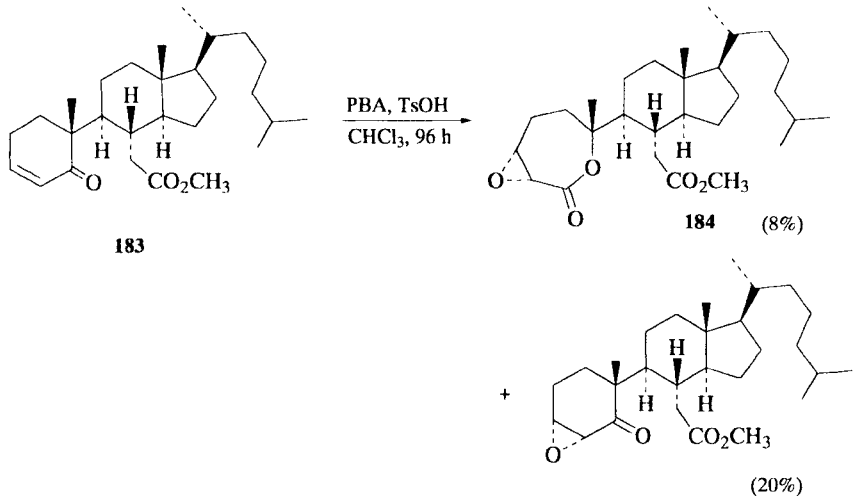
(Eq. 23)

The regiochemical outcome of the Baeyer–Villiger oxidation of cycloalkenones, in which the olefin and carbonyl group are parts of rings, depends upon substitution adjacent to the carbonyl group. Vinyl migration generally is preferred over methylene migration to give ring-expanded enol lactones,[492,493] as shown by the regioselective formation of lactone **182**.[493] Although epoxylactone **184** is formed from seco-

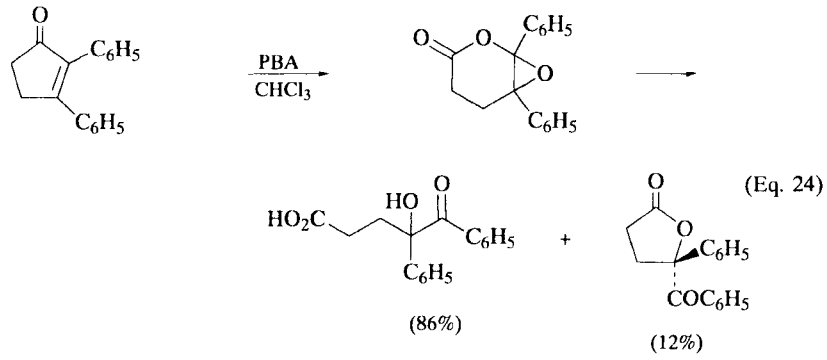


182 (68%)

cholestenone **183** by migration of the tertiary alkyl group, the yield is too low to infer a general principle for competitive migrations.[169]

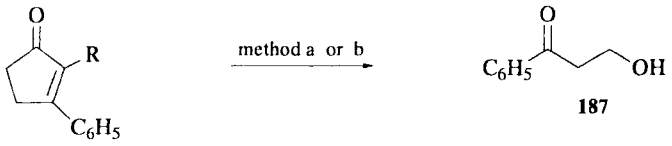


Potential problems during cycloalkenone oxidations include olefin epoxidation followed by rearrangements of the epoxylactone products (Eq. 24).[485] Further com-



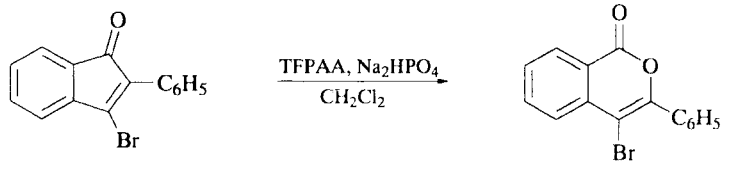
(Eq. 24)

plications may arise from base-catalyzed retrograde aldol condensations; keto acid **187** has been isolated following oxidation of cyclopentenones **185** and **186**.[485,494]



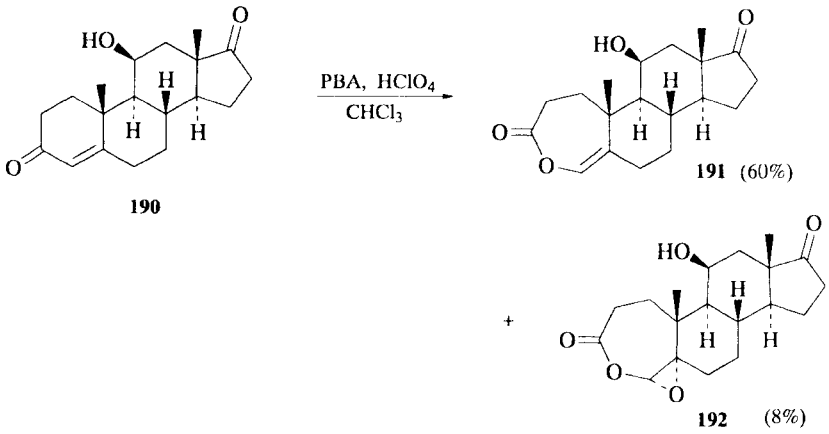
185	R = H	method a. PBA, $CHCl_3$	(50%)
186	R = CH_3	method b. 30% H_2O_2, NaOH, CH_3OH	(58%)

Oxidation of Fused-Ring Conjugated Ketones. Benz-fused cyclopentenone **188** affords lactone **189** by preferential vinyl migration.[493] Although the primary



188 **189** (82%)

Baeyer–Villiger oxidation product of a cycloalkenone flanked by a methylene group is usually an enol lactone formed by vinyl migration,[495] this product often is accompanied by a related epoxide.[281,298,305,496,497] An example is the chemoselective conversion of androst-4-en-3,17-dione **190** to enol lactone **191** and epoxylactone **192**.[281]

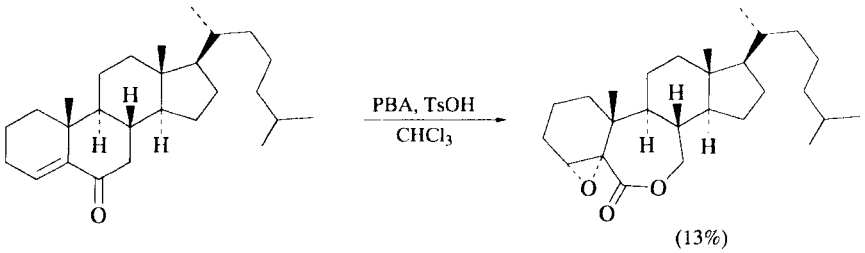


190

191 (60%)

\+ **192** (8%)

The general rule of preferential vinyl migration in the peracid oxidation of fused-ring cycloalkenones has exceptions. Major migration of a methylene group in preference to vinyl is observed in the perbenzoic acid oxidation of cholest-4-en-6-one to give an epoxylactone as the only Baeyer–Villiger product (Eq. 25).[498] Oxidation of

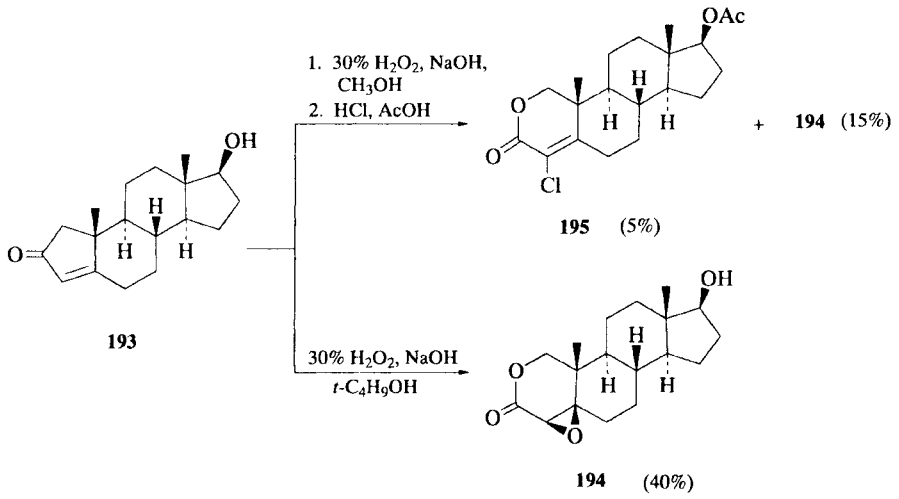


(13%)

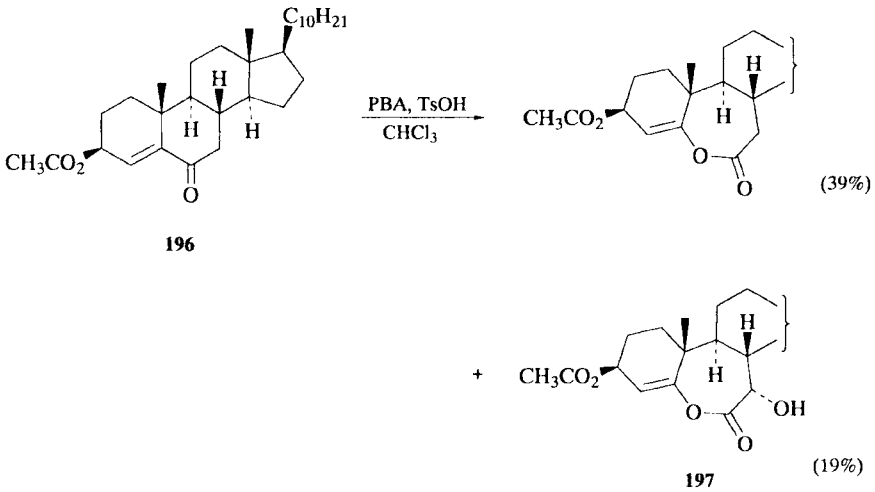
\+ products from the epoxidized olefin (48%)

(Eq. 25)

A-nortestosterone (**193**) with basic hydrogen peroxide affords epoxidized lactone **194** by way of methylene group migration;[299,499] the epoxylactone **194** isomerizes upon acid workup to α-chloro conjugated lactone **195**.



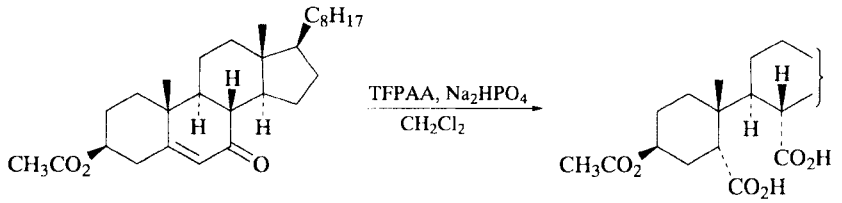
Alternative reactivity modes are potential problems with conjugated ketones. With perbenzoic acid the 3-β-acetoxyketone **196** gives a mixture containing an α-hydroxy enol lactone **197**, which can arise from epoxidation of the enol form of



the ketone followed by subsequent rearrangement.[500] Hydroxylation of the saturated carbon adjacent to the carbonyl is observed with other steroidal-4-en-6-ones,[303,501]

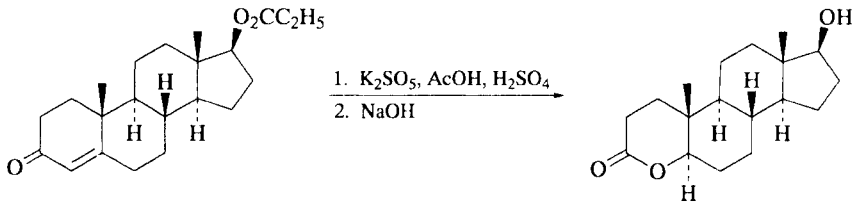
and with the triterpene 11-keto-α-amyrone.[502] In other cases only products derived from olefin epoxidation may be formed, as when steroidal 3,5-diene-7-ones react with perbenzoic acid or performic acid.[503,504]

Further oxidation of aldehydes formed in situ can lead to numerous products. If an initially formed enol lactone undergoes ring opening, peracid can oxidize the revealed aldehyde to an acid.[505] Cholestenone **198** oxidizes to diacid **199** even in



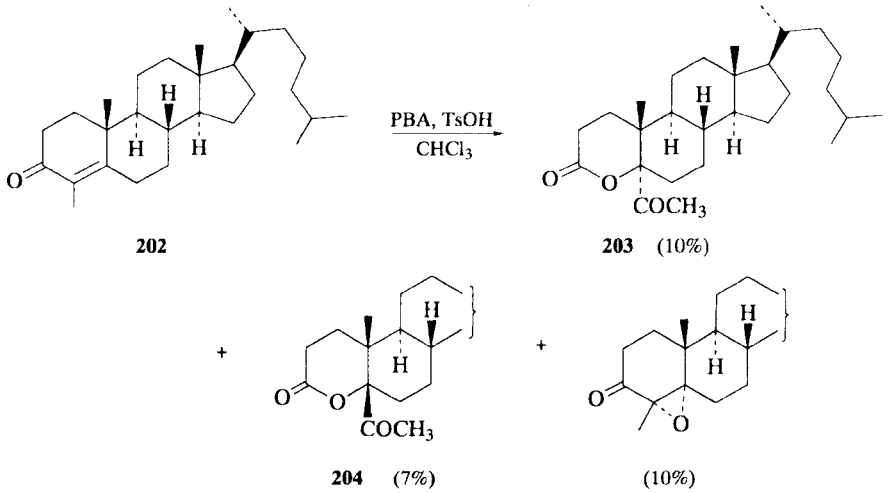
198 **199** (—)

buffered TFPAA.[506] An aldehyde can also undergo further Baeyer–Villiger oxidation to a formate ester.[252,507,508] Oxidation of **200** gives lactone **201**, which can be formed



200 **201** (26%)

by the conversions: enol lactone → aldehyde acid → formate ester acid → alcohol acid → lactone.[507]

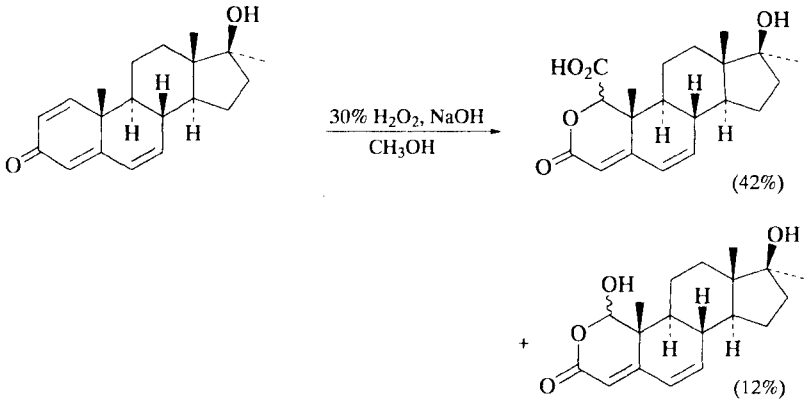


202 **203** (10%)

204 (7%) (10%)

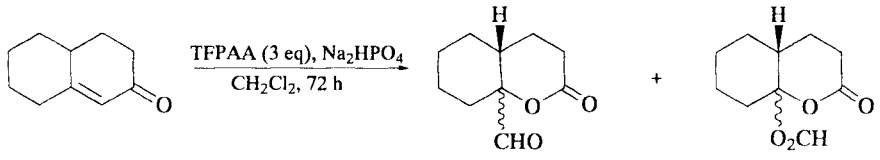
Ring opening of enol lactone epoxides in the presence of oxidant can result in a number of time- and peracid-dependent processes. The ring-opened α-hydroxy aldehyde or ketone can recyclize to a formyl- or acyl-substituted lactone.[298,504,508–513] An example is the ring opening and reclosure of the β-epoxy lactone formed during oxidation of cholestenone **202** to the mixture of acetyllactones **203** and **204**.[512]

Secondary oxidations of the α-hydroxyaldehydes, formed in situ from enol lactone epoxides, can occur. The aldehyde may oxidize to a carboxylic acid (Eq. 26).[514]



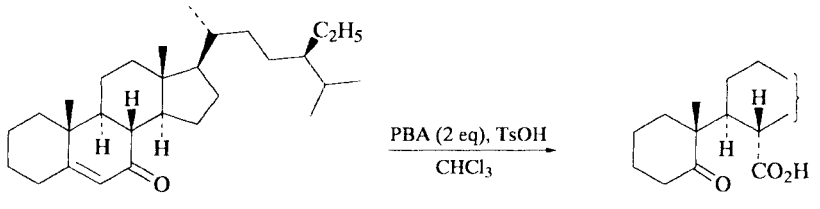
(Eq. 26)

Alternatively, as is shown in the oxidation of the unsaturated decalenone **205**,[298] an intermediate formyl lactone **206** can oxidize further to formate ester **207**.[298,508]



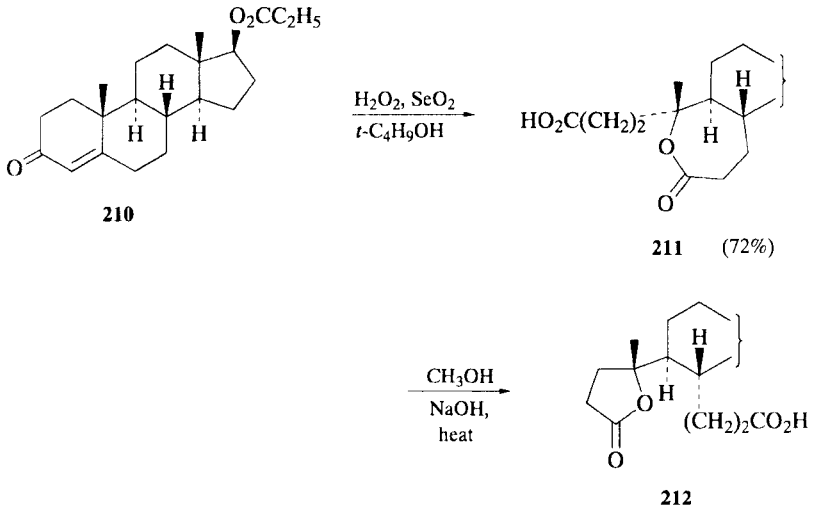
205 **206** (70%) **207** (30%)

If further hydrolysis occurs at the lactone formate ester oxidation level, the result is a ketoacid, which has lost one carbon as formic acid.[305,501,504,509,511,513] An example of this process is the oxidation of the B ring of stigmastenone (**208**) to ketoacid



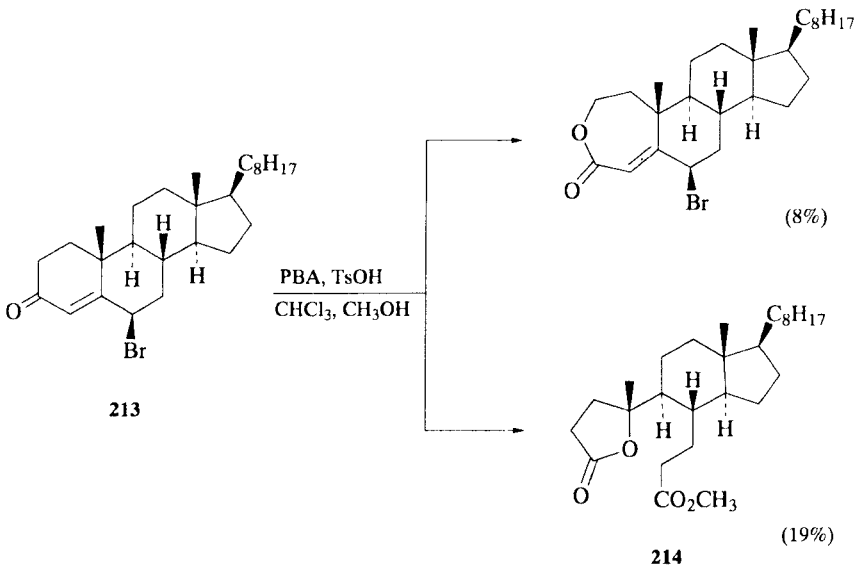
208 **209** (56%)

209.[504] The ketoacid formed in situ is subject to further Baeyer–Villiger reaction; the oxidation of testosterone propionate (**210**) shows conversion of the B ring to a lactone **211**, which is subject to ring opening and reclosure to lactone **212**.[101,508,515,516]

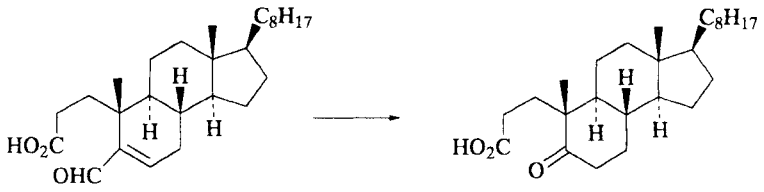


210 **211** (72%) **212**

The presence of a γ halogen can lead to products resulting from an elimination reaction. In the oxidation of bromoenone **213**, formation of an enol lactone followed by hydrolysis and elimination of hydrogen bromide forms an intermediate aldehyde **215**.[516] A second Baeyer–Villiger oxidation and hydrolysis of the enol formate ester

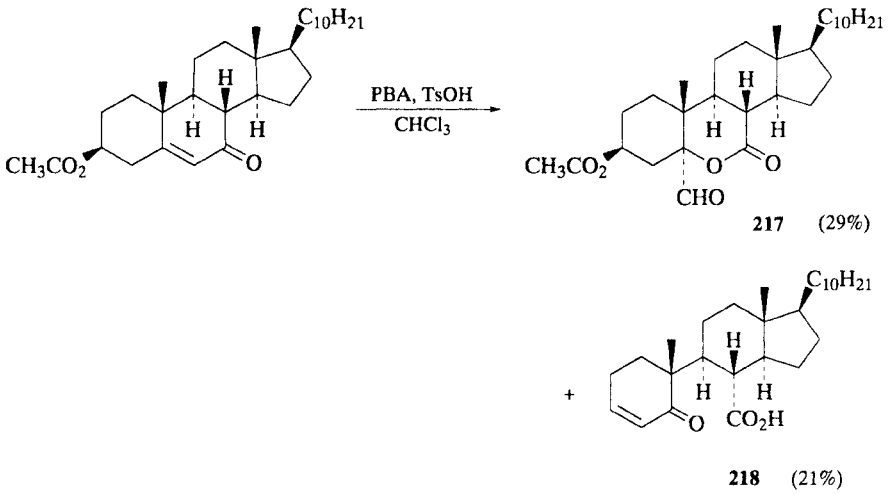


213 **214**



215 216

gives intermediate ketone **216**. A third Baeyer–Villiger oxidation with **216**, followed by ring opening and reclosure, provides lactone **214**. A homoallylic halogen or acetoxy group may also undergo elimination (Eq. 27).[504,511,513] Oxidation of the lactone



217 (29%)

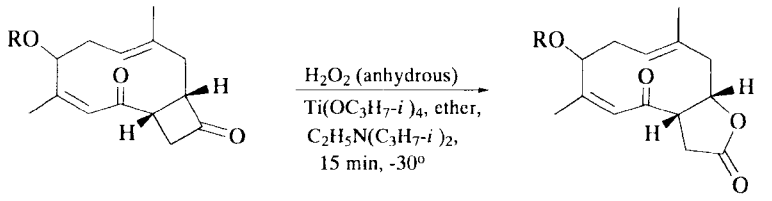
218 (21%)

(Eq. 27)

aldehyde **217** and hydrolysis of its derived hydroxyformate ester reveals a β-acetoxy ketone, which loses acetic acid to give enone **218**.[504]

The reactivity of cholest-5-en-7-one with MCPBA is reduced by a factor of 2–3 upon introduction of electron-withdrawing halogen or oxygen substituents at C-3-β.[517] A double bond also lowers reactivity, and 3-acetoxycholest-5-en-7-one is 15 times less reactive with MCPBA than 3-acetoxycholestan-7-one.[517] In molecules that contain conjugated and unconjugated ketones, the conjugated ketone often is either unreactive or is epoxidized. For example, in steroidal and triterpene ring systems perbenzoic acid effects Baeyer–Villiger oxidation at a C-3 carbonyl in preference to reaction with a 12-en-11-one functionality,[502] and a side-chain acetyl group can be converted to acetate with MCPBA in the presence of a hindered fused cyclohexenone.[108] Although 3β-acetoxy-16-allopregnene-12,20-dione reacts selectively with perbenzoic acid to give Baeyer–Villiger oxidation of only the 12-ketone with

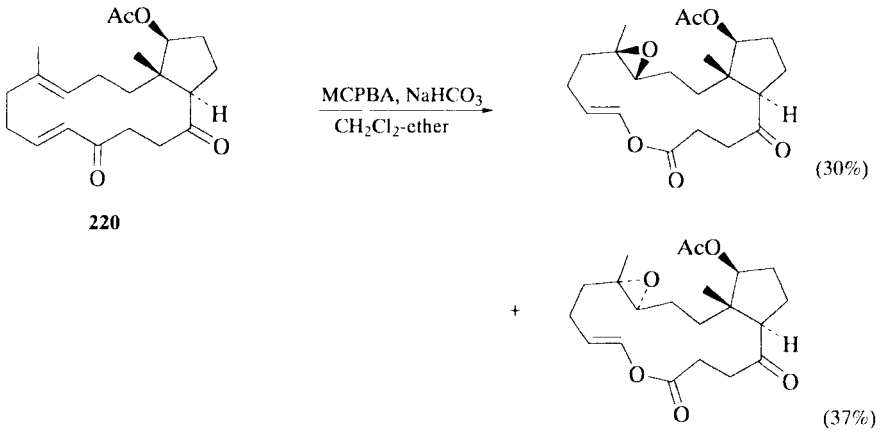
migration of C-13, α-epoxidation of the C-16 double bond also occurs.[518] A reactive cyclobutanone **219** can be selectively oxidized with basic anhydrous hydrogen peroxide in the presence of an isolated olefin and a conjugated ketone.[236]



219 (55%)

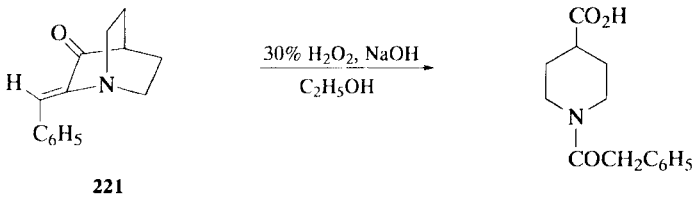
R = $C_6H_5CH_2OCH_2$

An example of selective Baeyer–Villiger oxidation of a conjugated ketone in the presence of a nonconjugated carbonyl is the MCPBA oxidation of diketone **220**. The reaction is accompanied by a nonstereospecific epoxidation of the isolated olefin.[519]

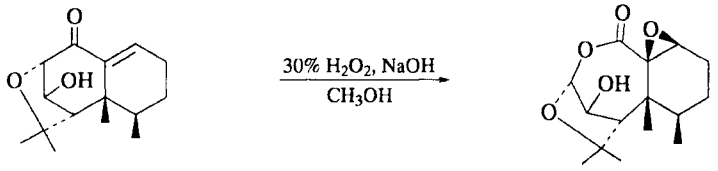


220 (30%) (37%)

Oxidation of Bridged-Ring Conjugated Ketones. Basic hydrogen peroxide oxidizes the bridged bicyclic ketone **221**, which has an *exo*-alkylidene group, so that cleavage occurs between the carbonyl and vinyl group.[520] However, the bridged ketone **147** affords an epoxylactone **222** in which the oxygen-substituted bridgehead



221 (40%)



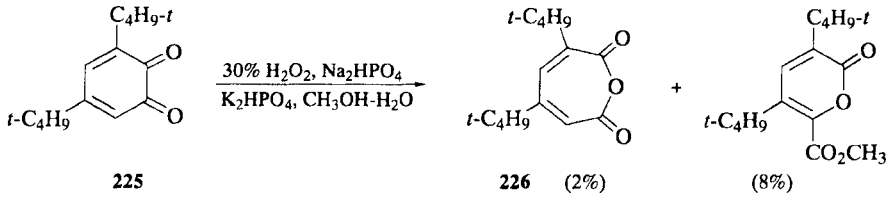
147 222 (43%)

has migrated.[433] Bridgehead migration without accompanying olefin epoxidation is reported in the MCPBA oxidation of tricycle **223** to the rearranged *exo*-methylenelactone **224**, whose putative structure is based upon ^1H NMR spectroscopy.[490]

223 224 (—)

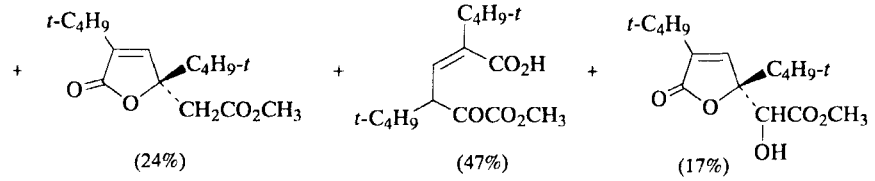
Reactions of 1,2-Dicarbonyl Compounds

Oxidation of α-diketones with MCPBA or monoperphthalic acid in inert solvents generally involves cleavage between the carbonyl groups to afford anhydrides,[218,490,521–527] while aqueous hydrogen peroxide[31,528–536] or aqueous workup of peracetic acid oxidations provide carboxylic acids.[537] In alcoholic solvents acid esters can be formed.[538,539] In the hydrogen peroxide oxidation of *o*-quinone **225** in methanol an initially formed anhydride **226** opens to an acid ester, which undergoes double bond oxidation and conjugate additions to give a mixture of products (Eq. 28).[31,525]



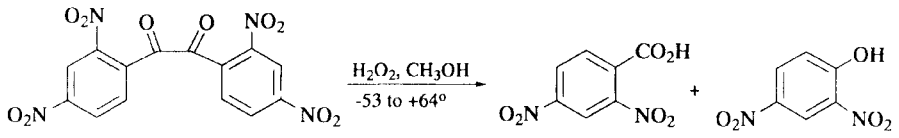
225 226 (2%) (8%)

(Eq. 28)



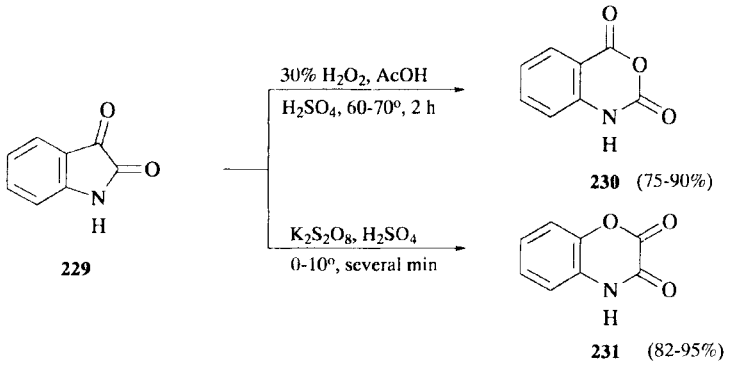
(24%) (47%) (17%)

Oxidation of 2,2',4,4'-tetranitrobenzil (**227**) with methanolic hydrogen peroxide provides temperature-dependent mixtures of aryl and carbonyl migrated products. More 2,4-dinitrophenol (**228**) is formed at higher temperatures.[540]



227 (30-60%) **228** (16-66%)

The regiochemistry of oxidation of α-ketoamide **229**, and numerous aryl derivatives containing electron-donating ether and alkyl groups, as well as electron-withdrawing halogen and trifluoromethyl groups, is dependent upon oxidant. Insertion between the carbonyl groups to give anhydride **230** is observed with 30% hydrogen peroxide/acetic acid/sulfuric acid, while insertion adjacent to the ring to give lactone **231** occurs with persulfuric acid.[541]



229

230 (75-90%)

231 (82-95%)

In a reaction which is part of the conversion of furan to L-ribofuranosides, tetrahydrofuranyl-α-ketoesters undergo regioselective migration of the carbon bearing the ring oxygen when oxidized with MCPBA (Eq. 29).[542,543] Acylphosphites,

(77%)

(Eq. 29)

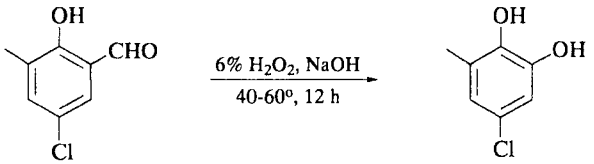
phosphorus analogs of α-keto esters, react with perbenzoic acid primarily to give acylphosphates (Eq. 30).[544]

$$C_6H_5COP(O)(OC_2H_5)_2 \xrightarrow[32°,\ 3\ d]{\text{PBA, benzene}} C_6H_5CO_2P(O)(OC_2H_5)_2 \quad (70\text{-}85\%)$$

(Eq. 30)

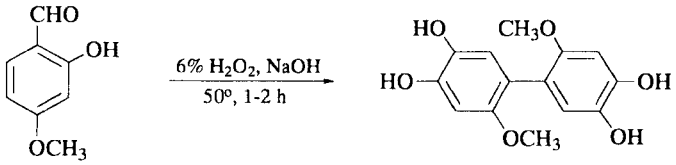
Reactions of Aldehydes

Oxidation of Aryl Aldehydes. Benzaldehydes containing hydroxy groups at the *ortho* or *para* position are converted to phenols by the Dakin oxidation using basic 3–6% hydrogen peroxide (Eq. 31).[96,545–556] Polycyclic aromatic *o*-hydroxy- or



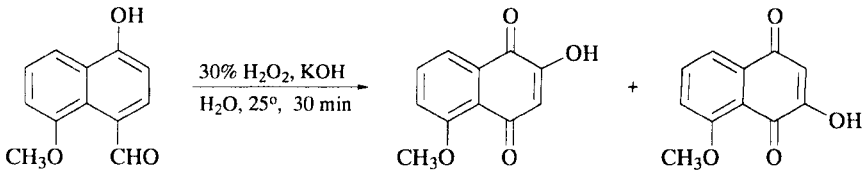
(72%) (Eq. 31)

p-hydroxyaldehydes also undergo the oxidation.[557–566] An example of aryl coupling has been reported when heating was employed with a reactive substrate (Eq. 32).[550]



(58-60%) (Eq. 32)

Stronger solutions of hydrogen peroxide (15–30%) are used occasionally;[567–570] however, oxidation to a quinone and ring hydroxylation may occur (Eq. 33)[571] Peracetic acid,[572,573] which gives major amounts of quinones by overoxidation, potas-

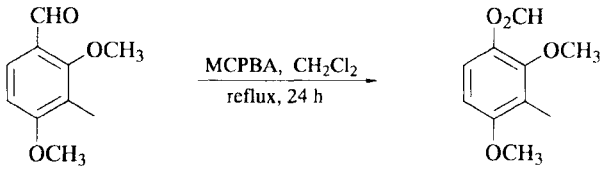


(73%)

(Eq. 33)

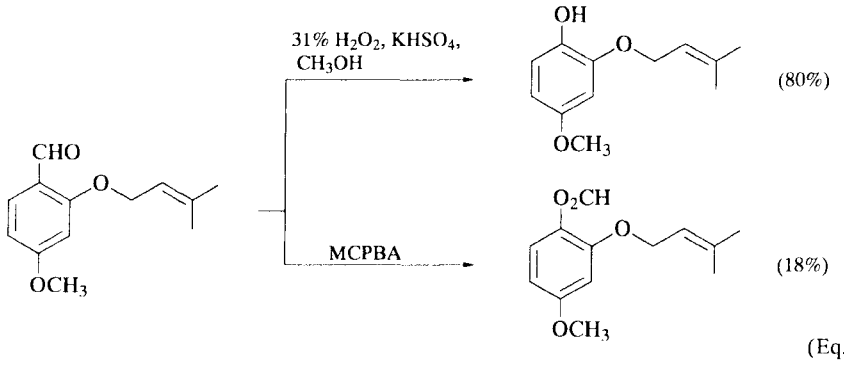
sium persulfate,[574] and MCPBA[575] are less effective oxidants for *o*-hydroxy- and *p*-hydroxybenzaldehydes.

Benzaldehyde or benzaldehydes that have *ortho* or *para* alkoxy substituents are not effectively oxidized by basic hydrogen peroxide to give phenols.[546,555] They can be oxidized to formate esters or the related phenols with 30% hydrogen peroxide catalyzed by areneseleninic acids,[576–578] acidic 31% hydrogen peroxide,[579] MCPBA,[575,580–599] TFPAA,[589] dinitroperbenzoic acid,[600] performic acid,[591,601–604] and peracetic acid.[572,573,605–609] A reaction used in the synthesis of mitomycin is shown in Eq. 34.[584,590,591] Quinone formation, which can accompany oxidation of *p*-methoxybenzaldehydes with peracetic acid,[572,573] is minimized by the use of lower reaction temperatures and shorter reaction times.[607]



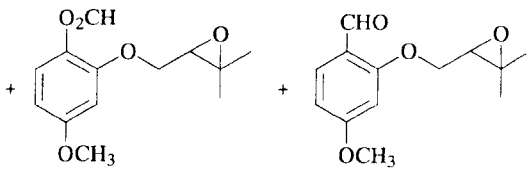
(96%) (Eq. 34)

Oxidation of reactive aromatic aldehydes with *O*-allyl side chains is chemoselective for Baeyer–Villiger oxidation with acidic 31% hydrogen peroxide[579] or MCPBA.[610] Epoxidation of an isopropenyl side chain accompanies formate ester formation with MCPBA, but not acidic hydrogen peroxide (Eq. 35).[579] Chemoselective



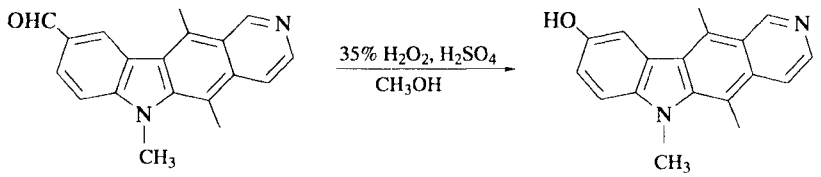
(80%)

(18%) (Eq. 35)



(30%) (40%)

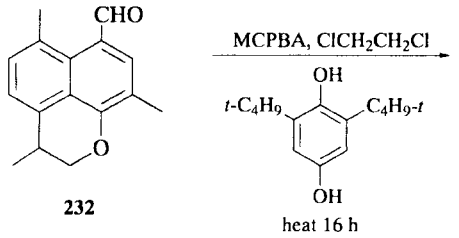
Baeyer–Villiger oxidations of reactive aromatic aldehydes are preferred over oxidation of pyridyl nitrogen in the presence of acidic 30–35% hydrogen peroxide (Eq. 36).[609,611]



(>90%)

(Eq. 36)

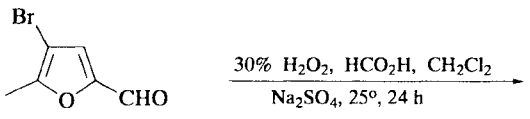
Steric hindrance toward attack of peracid on the formyl group precludes oxidation of naphthaldehyde **232**. TFPAA and MCPBA, even in refluxing 1,2-dichloroethane, fail to react.[612]



Complex mixture
+ starting material

Aromatic aldehydes which have *m*-methoxy[578,584] or *p*-methyl groups are best oxidized to phenols by 30% hydrogen peroxide containing *o*-nitrophenylseleninic acid (ONPSA).[578] Acidic 31% hydrogen peroxide gives mainly methyl esters with these substrates.[579] Phenols are obtained from benzaldehydes have a *p*-phenyl[577,578] or fused aromatic rings using *o*-nitrophenylperseleninic acid,[578,596] MCPBA,[571,613,614] or *p*-nitroperbenzoic acid.[615] Benzaldehyde is converted to benzoic acid by potassium persulfate.[574,589] Similarly, there are no reported Baeyer–Villiger oxidations of benzaldehydes substituted only by electron-withdrawing chloro or nitro groups; acidic hydrogen peroxide converts such aldehydes to benzoate esters.[579]

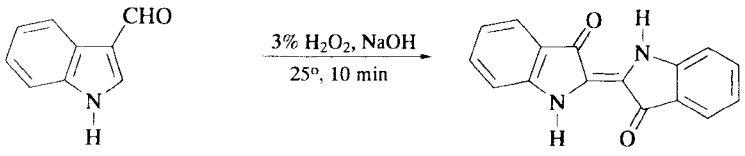
Electron-rich heterocyclic aldehydes which undergo the Baeyer–Villiger oxidation include 2-formylfurans, (Eq. 37),[616,617] *N*-(9)-methyl-3-formylcarbazole,[611] and *N*-



(Eq. 37)

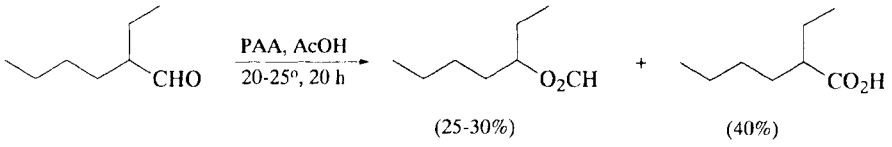
(69%)

(6)-methyl-9-formylellipticine.[611] A coupling product **234** is formed upon oxidation of 3-formylindole (**233**).[546] Electron-poor 3-formylisoquinoline is oxidized to the carboxylic acid by 30% hydrogen peroxide.[618]



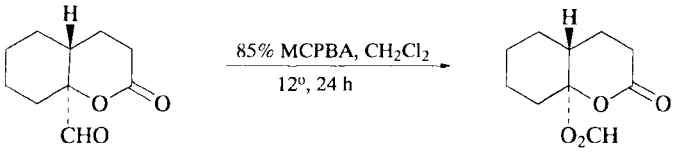
233 **234** (70%)

Oxidation of Alkyl Aldehydes. Primary aliphatic aldehydes are oxidized mainly to carboxylic acids by peracetic acid or MCPBA.[589,619] However, if the α-carbon is benzylic or secondary, formate ester formation generally is competitive with carboxylic acid formation using MCPBA,[620-622] peracetic acid,[589,623] or TFPAA as oxidants[589,619] (Eq. 38). An α oxygen facilitates formate ester formation (Eq. 39).[298]



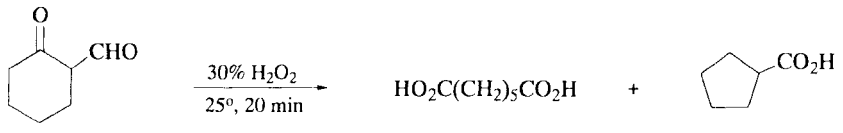
(25-30%) (40%)

(Eq. 38)



(Eq. 39)

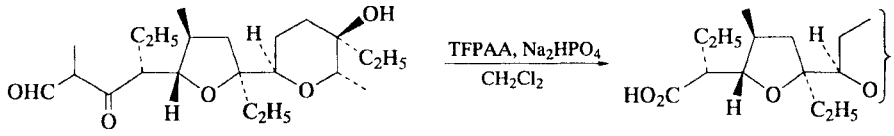
Oxidation of β-Ketoaldehydes. The oxidation of 2-formylcyclohexanones and 2-formylcycloheptanones by hydrogen peroxide affords a mixture of diacid and ring-contracted acid products (Eq. 40).[78,81,82,202-204,624] Shorter-chain diacids can be



(35%) (44%)

(Eq. 40)

observed.[202,204,625] Straight-chain β-ketoaldehydes and 2-formylcyclopentanones give only cleavage products.[202,203,624] A method for directed chain cleavage of an ethyl ketone toward the primary substituent involves formylation of its kinetic enolate and oxidative cleavage of the derived ketoaldehyde (Eq. 41).[80]

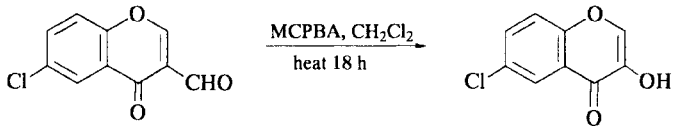


(79%)

(Eq. 41)

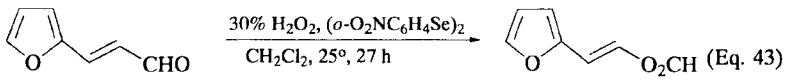
Reactions of α,β-Unsaturated Aldehydes

Baeyer–Villiger oxidation of α,β-unsaturated aldehydes to vinyl formates occurs with peracetic acid,[623,626] *p*-nitroperbenzoic acid,[627] and MCPBA.[600,628,629] An example is shown in Eq. 42.[629] A study of oxidations with 30 and 90% hydrogen



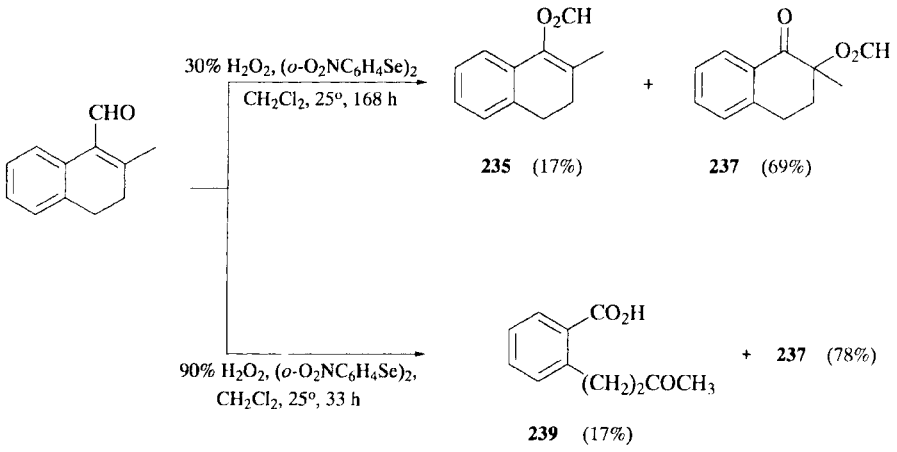
(85%) (Eq. 42)

peroxide catalyzed by benzeneseleninic acids found that *bis-o*-nitrophenyl diselenide is the most effective catalyst for vinyl formate formation; the furan ring and double bond are not oxidized under these conditions (Eq. 43).[628] This catalyst–oxidant combination appears to be the favored method for vinyl formate formation when comparisons with MCPBA have been made.[628]

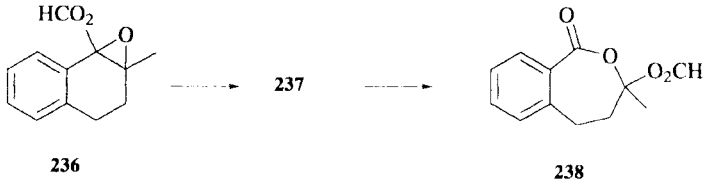


(53%) (Eq. 43)

Overoxidation may accompany Baeyer–Villiger oxidation (Eq. 44).[600,623,627] Epoxidation of vinyl formate **235** gives epoxyformate **236**, which rearranges to ketoformate **237**. Further oxidation gives formyloxylactone **238**, which hydrolyzes to ketoacid **239**.[600] Overoxidation is most usual after long reaction times and if peracids or 90% hydrogen peroxide catalyzed by arylseleninic acids are used as oxidants. Basic hydrogen peroxide converts unsaturated aldehydes mainly to epoxy formate esters,[627] unless the olefinic bond is especially unreactive as in formylazulene.[630,631]



(Eq. 44)



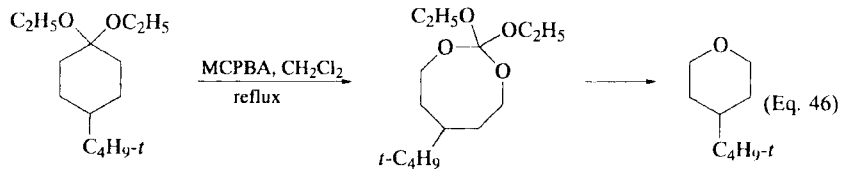
236 238

Peracid Reactions with Ketals and Acetals

Open-chain diethylketals can undergo a formal double Baeyer–Villiger oxidation to carbonate orthoesters upon treatment with MCPBA.[632,633] This oxidation results in a chain cleavage at both sides of the carbonyl carbon (Eq. 45).[632] Diethylketals of

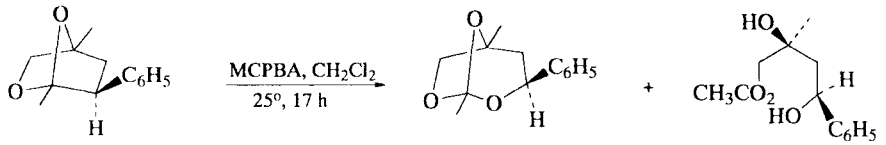
(Eq. 45)

cyclopentanones and cyclohexanones, but not cycloheptanones, are also converted by MCPBA to carbonate orthoesters;[632,633] these can rearrange to cyclic ethers if the reaction is carried out at reflux (Eq. 46).[632] Although cyclic ketals of ethylene glycol



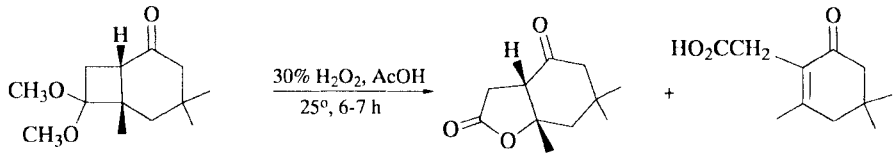
(Eq. 46)

are stable to this oxidation, bridged oxabicyclo[2.2.1]heptane ketal **240** is oxidized to the ortho ester level.[634,635]



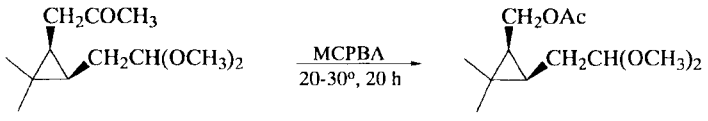
240 (53%) (26%)

Cyclobutanone dimethylketal **241** is oxidized chemoselectively to the butyrolactone **242** by aqueous peracetic acid.[111] Dimethylketals of cyclohexanone[232] and cyclopentanone[636] survive MCPBA during the oxidation of oxidizable carbonyl groups.

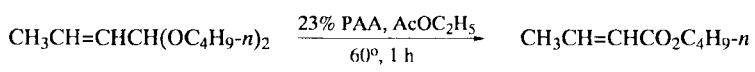


241 **242** (81% of a mixture)

Although the acetal function of **243** is less reactive than the methyl ketone side chain,[637,638] in the absence of a competing functionality a variety of acetals can be oxidized by peracids (Eq. 47)[639]. Aryl migration has been observed (Eq. 48)[579], but usually esters are formed by loss of the hydrogen atom of the aldehyde.[639] A one-step conversion of γ-lactol methylacetals to γ-butyrolactones utilizes MCPBA in boron trifluoride etherate.[640] The one-step oxidation of diacetal **244** to dilactone **245** is superior to a two-step hydrolysis and oxidation.[641] The oxidation is not useful for δ-lactols.[640]

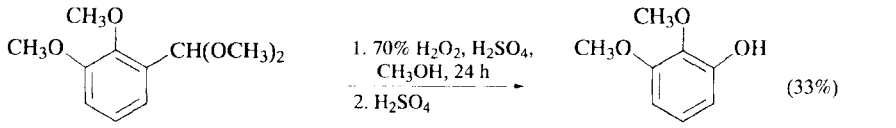


243 (75%)

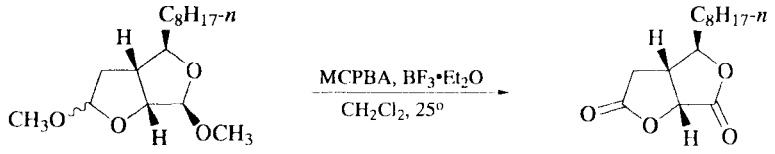


(70%)

(Eq. 47)



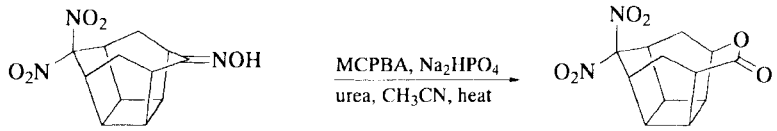
(Eq. 48)



244 **245** (80%)

Peracid Reactions with Nitrogen Derivatives of Ketones and Aldehydes

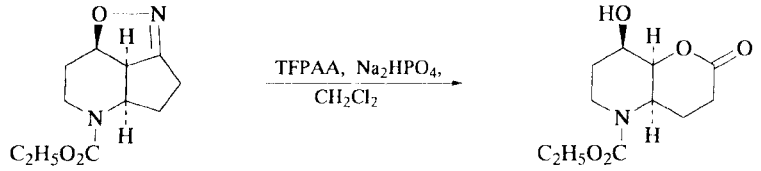
The Baeyer-Villiger oxidation can be carried out on nitrogen-containing ketone derivatives. Oximes of caged ketones are oxidized to lactones with 90% hydrogen peroxide/fuming nitric acid[439] or MCPBA (Eq. 49),[642] and peracetic acid or MCPBA



(52%)

(Eq. 49)

affords a lactone from the oxime of 5-α-3-cholestanone.[240,643] Isoxazolines are oxidized by excess TFPAA or 3,5-dinitroperbenzoic acid to lactones of β-hydroxyketones (Eq. 50).[85] Yields are comparable to those of a two-staged hydrogenolytic cleavage of the isoxazoline followed by Baeyer–Villiger oxidation.



(42%)

(Eq. 50)

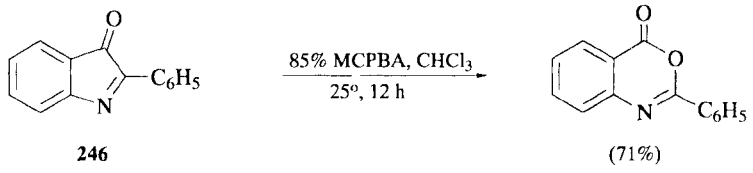
TFPAA effects cleavage of α-ketooximes primarily to diacids, although some oxidation of the oxime to a nitro group occurs (Eq. 51).[201] Oxygen is also inserted

$$C_6H_5COC(=NOH)CH_3 \xrightarrow[CH_2Cl_2,\ 1\ h]{TFPAA,\ Na_2HPO_4} \underset{(41\%)}{C_6H_5CO_2H} + \underset{(29\%)}{C_6H_5CO_2CH(NO_2)CH_3} + \underset{(5\%)}{C_6H_5O_2CCH(NO_2)CH_3}$$

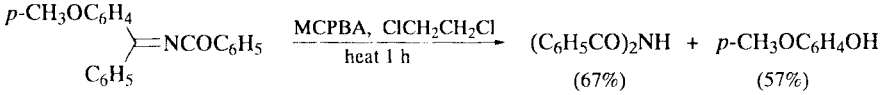
(Eq. 51)

between the ketone and imine double bonds upon treatment of 3-oxoindolenine **246** with 35% hydrogen peroxide[644] or MCPBA.[645]

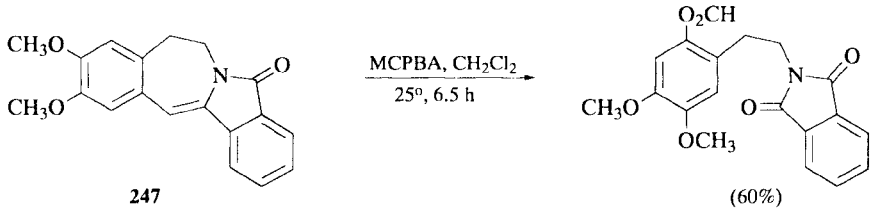
N-Benzoyldiarylimes are oxidized to a mixture of phenol and imides (Eq. 52).[646] An attempt to prepare an epoxide of an *N*-acylenamine **247** led to oxidative ring



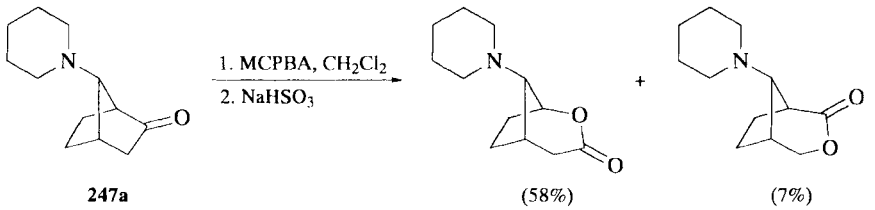
246 (71%)



(Eq. 52)

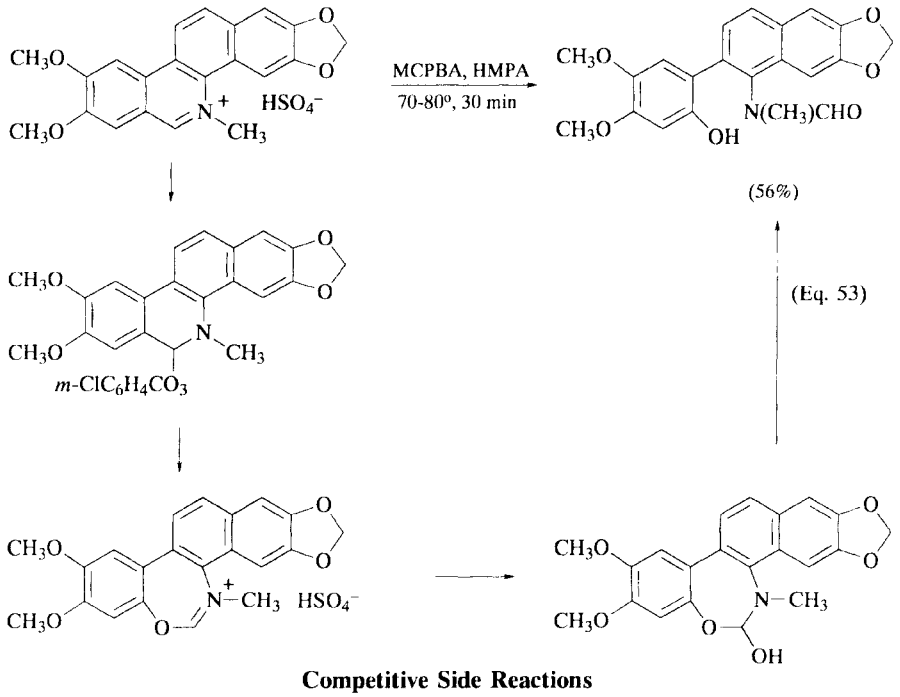


247 (60%)



247a (58%) (7%)

opening and Baeyer–Villiger oxidation of the released arylaldehyde.[597] *N*-Alkyliminium ions of amines and aryl aldehydes also react with MCPBA to form arylformate esters, most probably as shown in Eq. 53.[647,648] The weaker oxidant *N*-benzoylperoxycarbamic acid does not form Baeyer–Villiger products with azines or imines.[649]

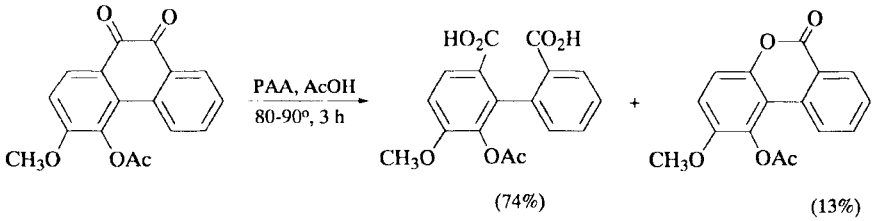


Competitive Side Reactions

Reactions of substrates to give products other than those of the normal Baeyer–Villiger oxidation are considered to be side reactions for purposes of this section. Side reactions can occur because of the oxidizing nature of the Baeyer–Villiger reagent, the acidic or basic nature of the reaction medium, or the reaction workup conditions. In prior sections of this review, where applicable, oxidations of double bonds, nitrogen, sulfur, and selenium atoms have been discussed.[2] Baeyer–Villiger oxidation of amine-containing substrates have been reported with and without *N*-oxide formation; for example, the piperidinyl group of *anti*-7-(1-piperidinyl)bicyclo[2.2.1]heptan-2-one (**247a**) is almost immediately oxidized by MCPBA to its *N*-oxide, whereas a reductive workup using sodium hydrogen sulfite is necessary to obtain the mixture of aminolactones.[371c] Separate sections of this review have been devoted to oxidations of carbon–nitrogen double bonds and to ketals and ketones formed by loss of the ketal protective group. Rearrangements and subsequent oxidations during Baeyer–Villiger oxidation of α,β-unsaturated ketones have been discussed in the section devoted to those ketones. Other oxidative and rearrangement processes occasionally observed are discussed here.

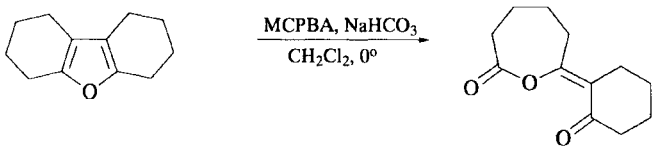
There are less common oxidative processes that can accompany or defeat the desired Baeyer–Villiger oxidation. Ketone enolates can undergo olefin epoxidation to provide α-hydroxyketones.[70,303,501,502] MCPBA is capable of oxidizing secondary alcohols to ketones.[2,650] Persulfate ion hydroxylates formyl or acyl substituted phenols and arylamines.[651] Benzaldehyde and aromatic ketones can be hydroxylated by hydrogen peroxide catalyzed by antimony pentafluoride–hydrogen fluoride without Baeyer–Villiger oxidation.[652] Occasionally electrophilic attack by MCPBA or per-

acetic acid occurs at an *ipso* position with resulting loss of the *ipso* substituent (Eq. 54).[320,537] Furans can undergo oxidative cleavage with MCPBA (Eq. 55).[653-655]



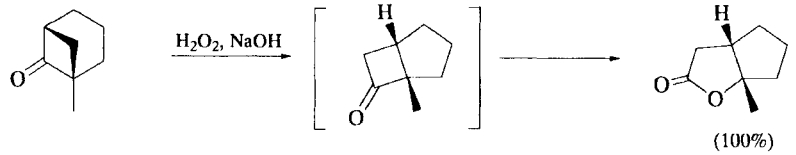
(74%) (13%)

(Eq. 54)



(92%) (Eq. 55)

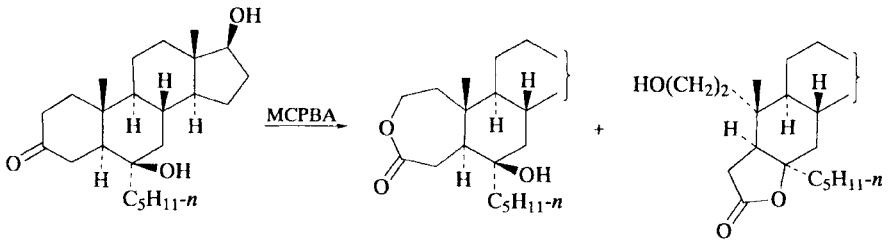
Baeyer–Villiger catalysts can epimerize[63,154] or rearrange[226] ketone substrates. An example of structural rearrangement in basic hydrogen peroxide is shown in Eq. 56.[656] Sensitive functional groups may be altered. Silyl protecting groups



(100%)

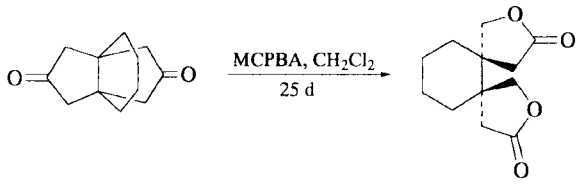
(Eq. 56)

usually survive treatment with buffered peracids, but partial loss of *O-tert*-butyldimethylsilyl groups is reported;[53,58] *O-tert*-butyldiphenylsilyl is more stable to peracid.[53] Acid-catalyzed ester exchange between the acid of the peracid and the product ester[58,657,658] is minimized by using a buffer such as disodium hydrogen phosphate, common in trifluoroperacetic acid oxidations.[15,42] Intramolecular ester exchange of hydroxy lactones[355] (Eq. 57)[659] or dilactones (Eq. 58)[660] occurs even in



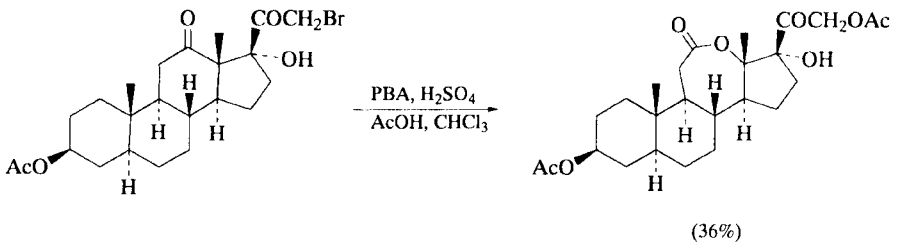
(51%) (25%)

(Eq. 57)



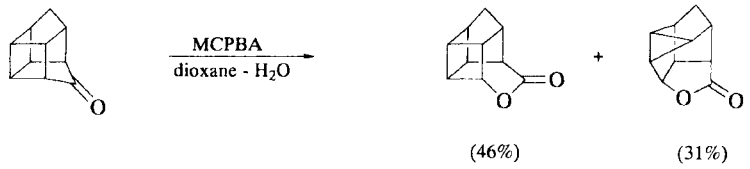
(Eq. 58)

the presence of buffer, although acid catalysis accelerates the exchange. Lactone formation can follow the basic hydrolysis of an acetate ester.[63,91,661] Reactive halides may be converted to esters by displacement with acid nucleophiles (Eq. 59).[282]



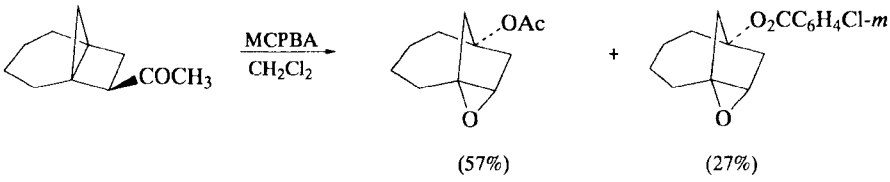
(Eq. 59)

The combination of ring strain and acidic catalysts is conducive to formation of cationic rearrangement products from lactones. A commonly observed process upon oxidation of strained cyclobutyl ketones is rearrangement of the derived cyclobutanol ester[658,662] or lactone[364,379,663,664] to a cyclopropyl carbinyl isomer (Eq. 60).[377]



(Eq. 60)

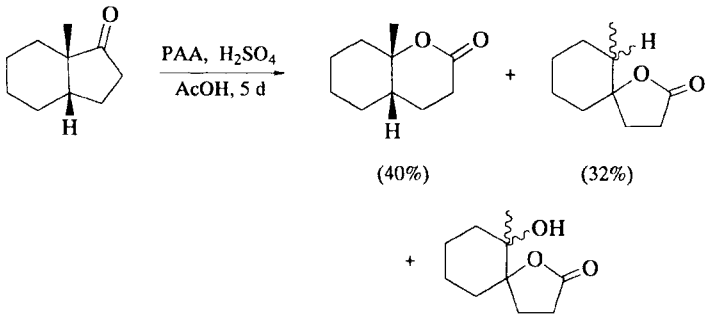
This process can occur even if the oxidation is carried out with buffered peracid.[658] The rearrangement of cyclopropylcarbinyl esters to 4-butenyl esters[52,662,665] can be accompanied by epoxidation of the double bond (Eq. 61).[657]



(57%) (27%)

(Eq. 61)

The combination of a strongly acidic reaction medium and the lactone or ester of a tertiary alcohol may generate a tertiary cation, which can behave in a number of ways. Alkyl shifts[440,666] and hydride shifts (Eq. 62)[667] can afford rearranged lac-

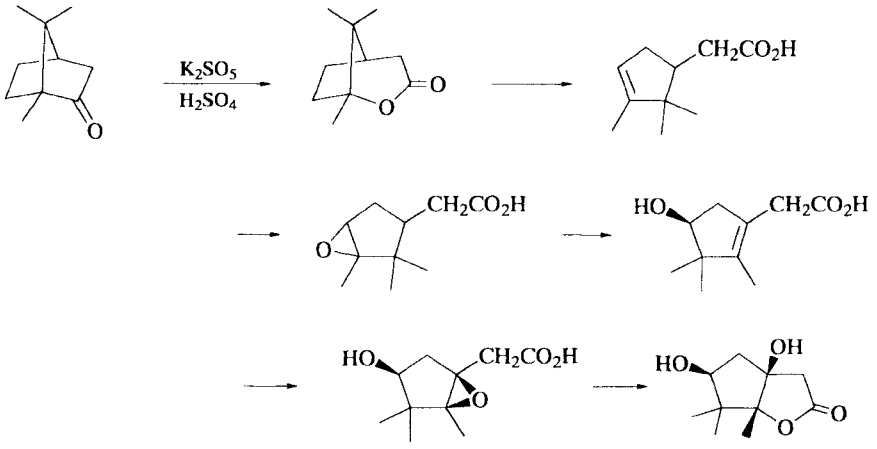


(40%) (32%)

(Eq. 62)

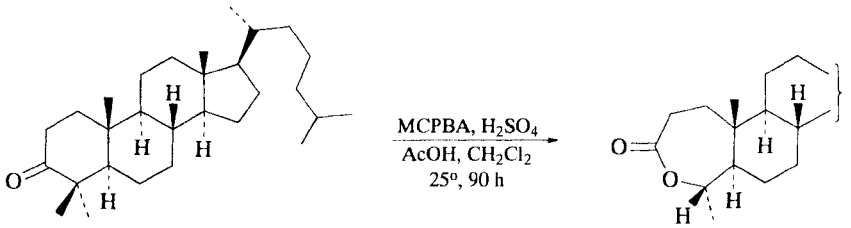
248 (28%)

tones. Olefins formed by proton loss from cations can be further oxidized by peracid;[667] hydroxylactones **248**[667] and **249**,[668] the latter a side product from camphor oxidation, are examples of rearranged and overoxidized Baeyer–Villiger products.



249 (10-15%)

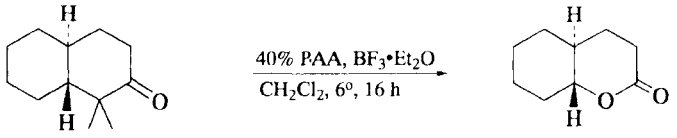
Oxidation of 4,4-dimethylcholestan-3-one (**250**) with MCPBA in the presence of 10% sulfuric acid/acetic acid results in loss of a methyl group (Eq. 63).[251,669,670] This



250 (65%)

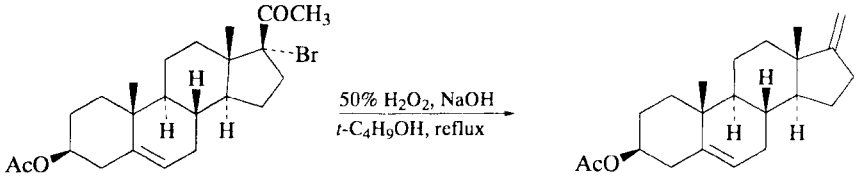
(Eq. 63)

process, which involves acid-catalyzed ring opening, elimination, and further oxidations, has been modified with boron trifluoride and 40% peracetic acid into a synthetically useful procedure for "exhaustive" Baeyer–Villiger oxidations of α,α-dimethyl fused ring ketones to give lactones (Eq. 64).[284,285,622,671] The latter are convertible to enones.[285]



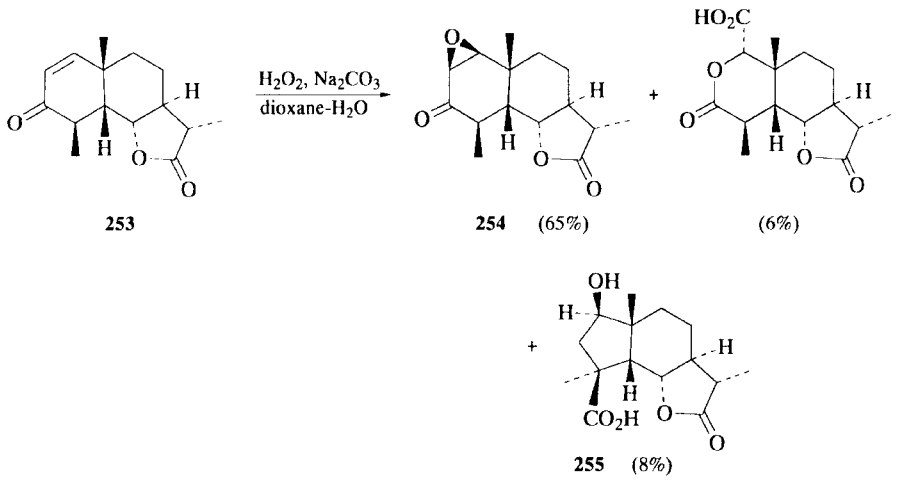
(36%) (Eq. 64)

The α-bromoketone **251** reacts with basic hydrogen peroxide by a Favorskii process to give a cyclopropanone, which upon trapping with peroxide anion liberates carbon dioxide and olefin **252**.[672] A Favorskii rearrangement of the epoxyketone

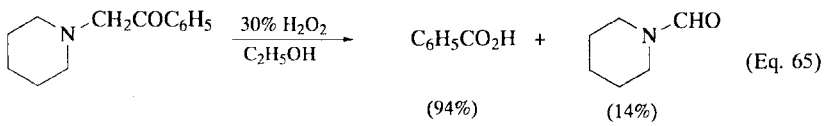


251 **252** (65%)

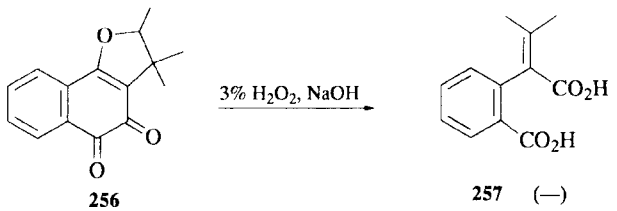
254, during basic hydrogen peroxide oxidation of α,β-unsaturated ketone **253**, provides the ring contracted acid **255**.[673] Hydrogen peroxide causes oxidative fragmentation of α-*N*,*N*-dialkylaminoketones (Eq. 65).[73] Dunnione (**256**) is somehow fragmented and rearranged by basic hydrogen peroxide to give the diacid **257**.[674]



253 254 (65%) (6%) 255 (8%)

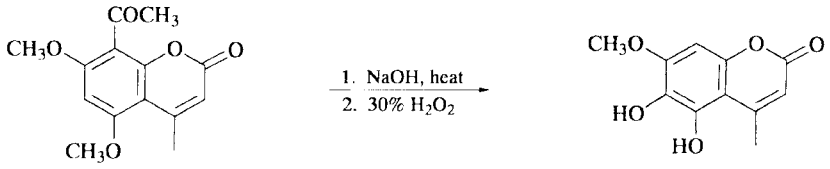


(94%) (14%) (Eq. 65)



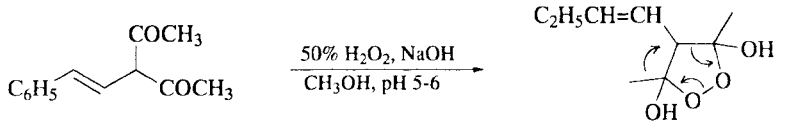
256 257 (—)

As discussed in the section on aldehyde oxidations, oxidation to a carboxylic acid can compete with the Baeyer–Villiger oxidation.[584] In the reaction of aryl aldehydes, a further side reaction in the Baeyer–Villiger oxidation is in situ hydrolysis of the formate ester to a phenol, which is further oxidized to a quinone [See Eq. 32].[571,572,675] Less usual is selective demethylation of a methoxy group; the rearranged coumarin **259** is formed during the Dakin oxidation if the acetyl coumarin **258** is preheated with base to open the lactone ring to form a *trans*-cinnamic acid.[676]

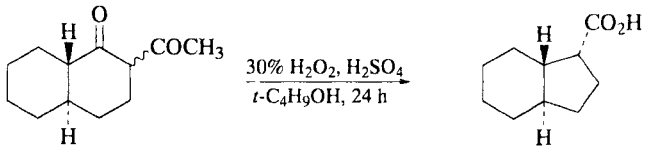


258 259 (59%)

Rearrangement, rather than Baeyer–Villiger oxidation, of 1,3-diketone **260** to give acid **261** occurs with basic hydrogen peroxide.[677] Similarly, ring contraction of α-acyldecalones occurs upon treatment with acidic hydrogen peroxide (Eq. 66).[82]

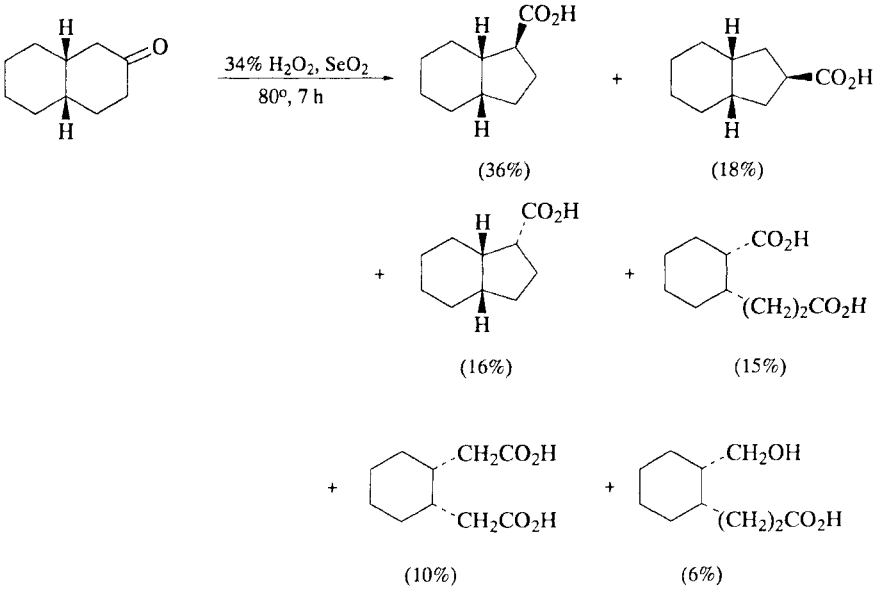


260 **261** (70%)



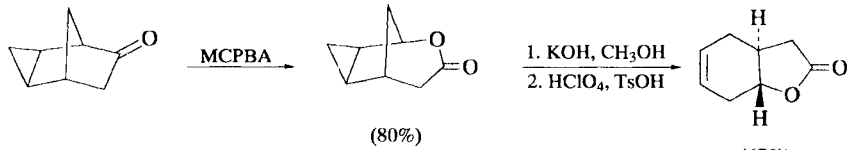
(92%) (Eq. 66)

Cyclic ketones can be oxidized by hydrogen peroxide in the presence of selenium dioxide to give ring-contracted acids; these are accompanied by diacids and hydroxy acids derived by ring opening and further oxidation of the lactones formed by Baeyer–Villiger oxidation (Eq. 67).[678–680]



(Eq. 67)

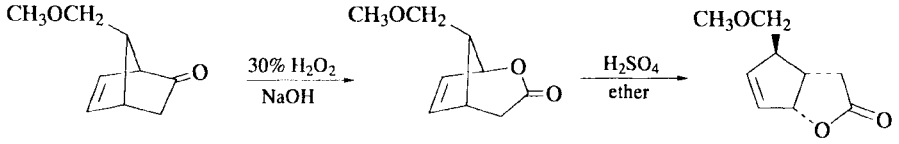
Rearrangements of Baeyer–Villiger products can be carried out during the reaction workup. The solvolysis of cyclopropyl carbinols prepared by the Baeyer–Villiger reaction has been developed into an efficient and stereoselective route to fused-ring γ-butyrolactones (Eq. 68).[422] Allylic rearrangement of bridged bicyclic lactones is



(80%) (67%)

(Eq. 68)

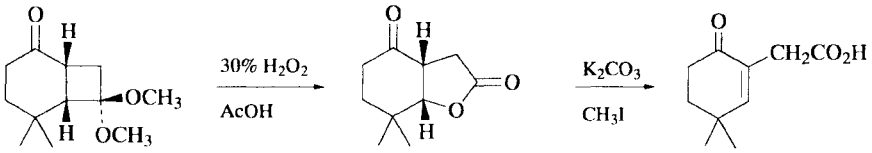
useful in the stereocontrolled synthesis of substituted cyclopentenes[60,414–416,681] and cyclohexenes.[423] The acid-catalyzed rearrangement, although useful in the synthesis of prostaglandin precursors (Eq. 69),[395,681] can be avoided if the lactone is opened



(95%)

(Eq. 69)

with base and the carboxylate anion is converted to the ester.[389] Lactones of β-hydroxycyclohexanones are converted to substituted cyclohexenones upon treatment with sodium hydroxide;[423] the reaction is part of a method for α-carbalkoxymethylation of α,β-unsaturated ketones nonenolizable toward the γ position (Eq. 70).[111]



(41%)

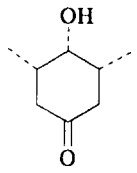
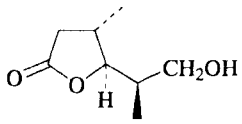
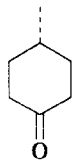
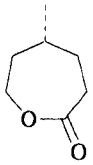
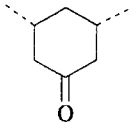
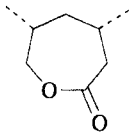
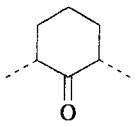
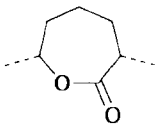
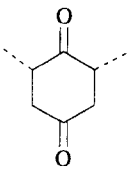
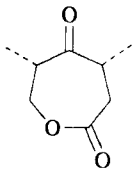
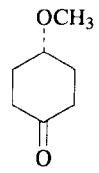
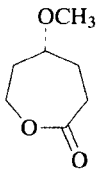
(Eq. 70)

Alternative Methods

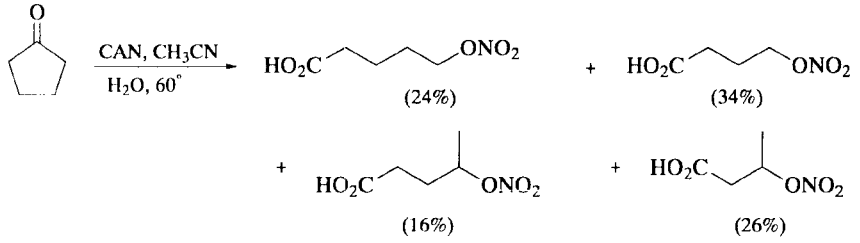
Biological Methods. Although the biological Baeyer–Villiger oxidation is not included in the tabular portion of this review, microorganisms are capable of converting ketones to lactones.[172,682–684] Enantioselective enzymatic conversions of mesomeric cyclohexanones to lactones with cyclohexanone monooxygenase

(EC 1.14.13.-) are shown in Table 7.[685] The enzyme is extremely efficient at discriminating between the two sides of the carbonyl group. The analogous enantioselective Baeyer–Villiger reaction using chemical rather than biological chiral reagents has not been reported.

TABLE 7. ENZYMATIC OXIDATION OF SELECTED *MESO*-CYCLOHEXANONES

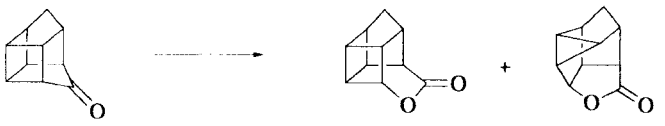
Substrate	Product	Yield (%)	ee (%)
		88	>98
		80	>98
		73	>98
		27	>98
		25	>98
		76	75

Non-Peracid Oxidants. The Baeyer–Villiger reaction is normally defined as the conversion of a ketone to a lactone with a peracid or other peroxy compound. The same transformation to lactones or related cleavage products can be effected using other oxidizing agents. Ceric ammonium nitrate (CAN) cleaves cyclopentanones and cyclohexanones; however, the reactions can be accompanied by rearrangements and chain shortening (Eq. 71).[686] Bridged ketones in which the carbonyl is part of a

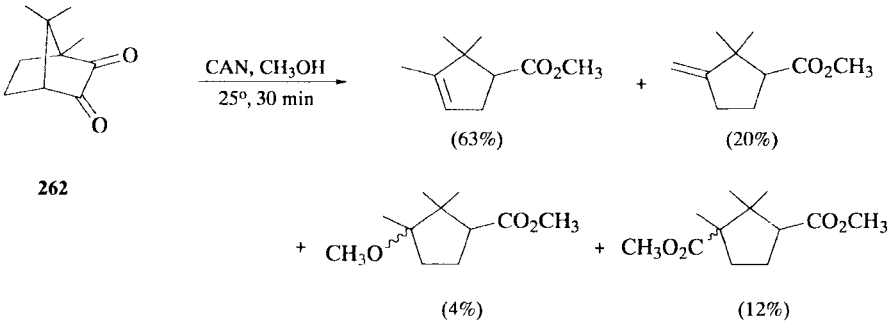


(Eq. 71)

strained ring can be oxidized to lactones with ceric ammonium nitrate in acetonitrile,[378,380,687–689] or lead tetraacetate in pyridine/benzene;[377,690] however, rearrangements are more prevalent with these oxidants than during Baeyer–Villiger oxidations with MCPBA (Eq. 72)[380] Bridged 1,2-diketone **262** reacts with ceric ammonium nitrate to form a mixture of products.[691]

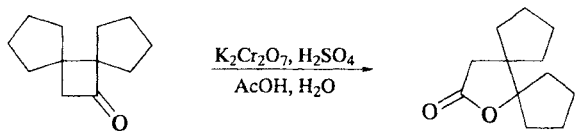


(Eq. 72)



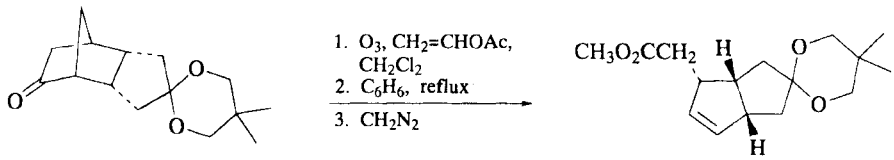
262

Chromic acid oxidation of cyclobutanones flanked by a secondary or tertiary alkyl group leads to butyrolactones;[692–695] an example is shown in Eq. 73.[694]



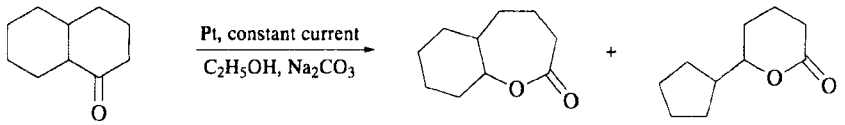
(70%) (Eq. 73)

Ozonolysis of vinyl acetate generates formaldehyde oxide ($CH_2{=}O^+{-}O^-$), which reacts with ketones to give lactones or related cleavage products (Eq. 74).[696] Anodic oxidation of ketone **263** affords mainly rearranged lactone **264**.[697]



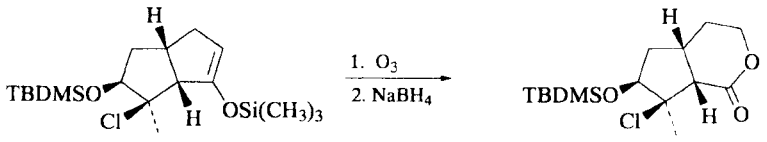
(51%)

(Eq. 74)



263 (14%) **264** (47%)

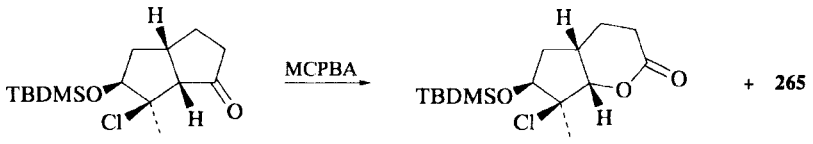
Oxidation of Ketone Derivatives. Enolsilanes, which can be prepared with regiocontrol,[698,699] form lactones following reductive workup of the product of ozonolysis. This method is complementary to the Baeyer–Villiger reaction in that it allows oxygen to be introduced at the less substituted carbon.[698,700] The utility of the method in the preparation of lactone **265** is shown in Eq. 75. Baeyer–Villiger oxida-



265 (20%)

(Eq. 75)

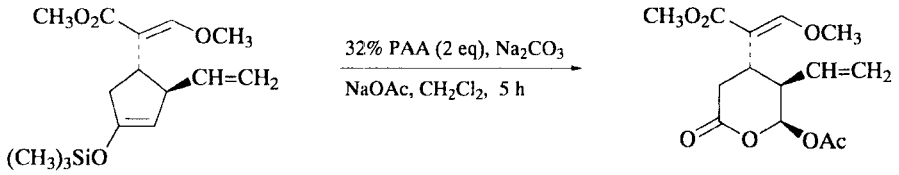
tion of fused ketone **266** with MCPBA favors bridgehead migration and affords an 80:20 mixture of lactones **267** and **265**.[701]



266 **267**

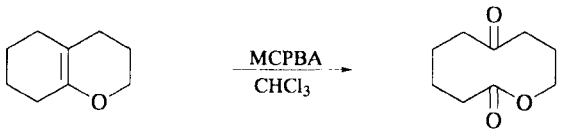
267 : 265 = 80 : 20

Epoxidation of enol silanes followed by rearrangement leads to α-acyloxyketones, which are subject to Baeyer–Villiger oxidation. Treatment of enol silane **268** with excess peracetic acid yields in chemoselective and regioselective fashion the acetoxylactone **269**.[702]



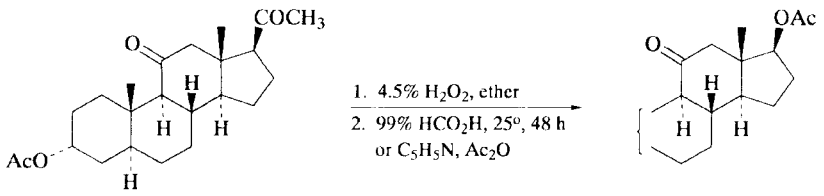
268 **269** (71%)

Methyl ketones generally undergo a two-carbon chain shortening to give acetate esters under Baeyer–Villiger conditions; however, formation of a terminal enol silane and ozonolysis converts a methyl ketone to a carboxylic acid of one less carbon.[698] Enol acetates can be used in place of enol silanes.[703] Fused enol ethers[704–712] and fused furans[713] can be cleaved to ketolactones with MCPBA (Eq. 76).[704]



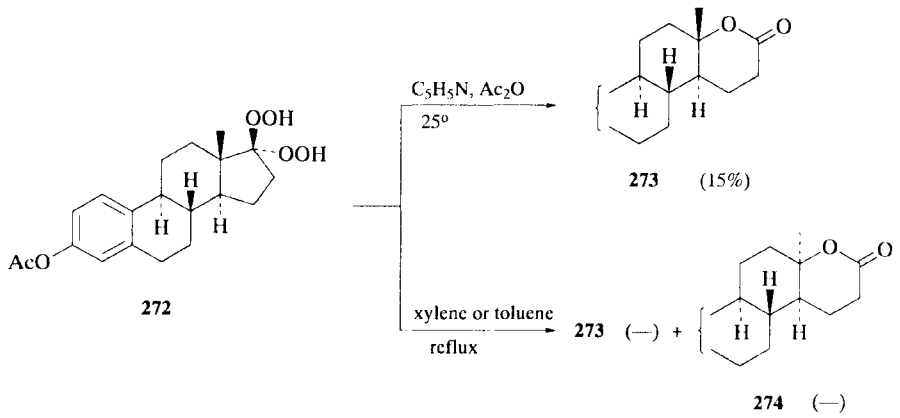
(67%) (Eq. 76)

A reaction which is similar to the Baeyer–Villiger oxidation is the *reaction of* ketones with ethereal 4–8% hydrogen peroxide and subsequent rearrangement of the bis-hydroperoxide adducts to lactones by pyrolysis in refluxing solvent,[714] or treatment with anhydrides[714,715] or acids.[716] By this method the C-20 ketone **270** is converted chemoselectively to the 17-acetoxysteroid **271**.[715,716] Epimerization at C-13



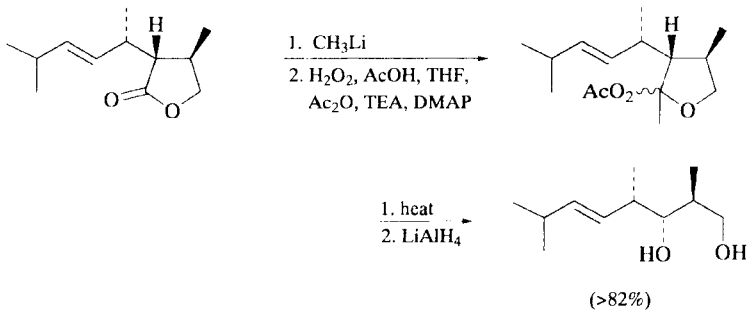
270 **271** (15%)

occurs when the bis-peroxide **272** is converted to lactones **273** and **274** by refluxing in xylene or toluene.[714]



272 **273** (15%) **273** (—) + **274** (—)

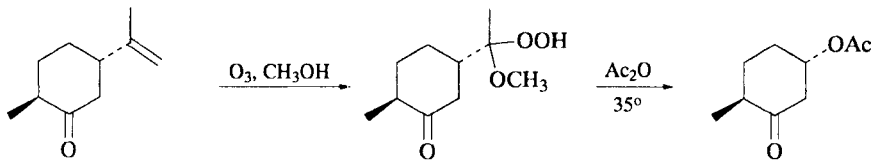
Related to the rearrangement of bis-hydroperoxides is the rearrangement sequence of lactones to diols shown in Eq. 77.[717–719] Rearrangement of the acylated α-alkoxy



(>82%)

(Eq. 77)

hydroperoxide is effected by heating.[720] Since α-alkoxyhydroperoxides can be formed by ozonolysis of olefins, the method of Eq. 78 can be a useful complement to the Baeyer–Villiger oxidation in Eq. 79.[110]



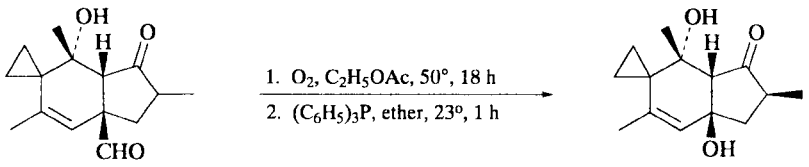
(79%)

(Eq. 78)

(79%)

(Eq. 79)

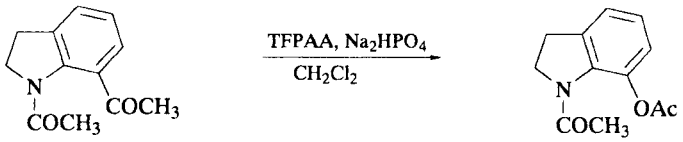
A mild chemoselective method for oxidative deformylation involves conversion of an aldehyde to a hydroperoxide with oxygen, followed by rearrangement and subsequent reduction.[721] This method was useful for a chemoselective oxidation of the sensitive substrate **275**.[721]



275

(37%)

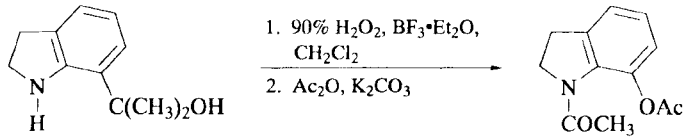
Baeyer–Villiger oxidation of highly electron-rich acetophenones with one or two groups *ortho* to acetyl often is difficult with peracids (Eq. 80). In such cases



(20-25%)

(Eq. 80)

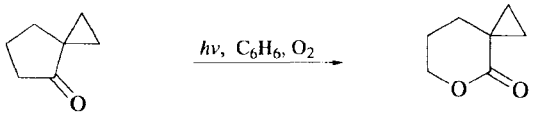
phenols often can be prepared by rearrangement of secondary or tertiary benzylic hydroperoxides, which can be derived from the corresponding acetophenone or benzoate ester (Eq. 81).[722,723] The method also is useful for aromatic substrates, such as



(57%) (Eq. 81)

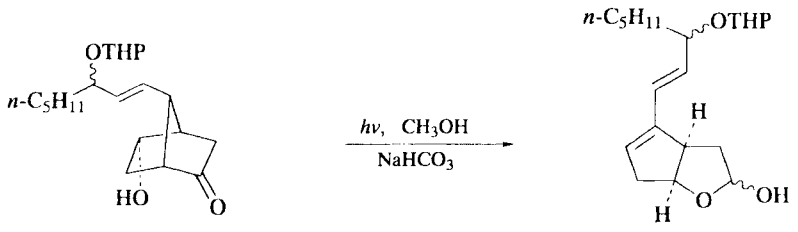
indolines, which undergo secondary reactions at the expense of the Baeyer–Villiger reaction.

Photochemical Methods. If certain structural requirements are met, it is possible to expand cyclic ketone rings photochemically to hemiacetals, which can be oxidized to lactones.[350,724–727] Photochemical oxidative expansions of cyclobutanones are aided by α substitution, and insertion of oxygen occurs with retention of stereochemistry at the migrating center.[229,724,728] Irradiation of spirocyclopentanone **276** in the presence of oxygen gives lactone **277**.[724] The method provides lactones



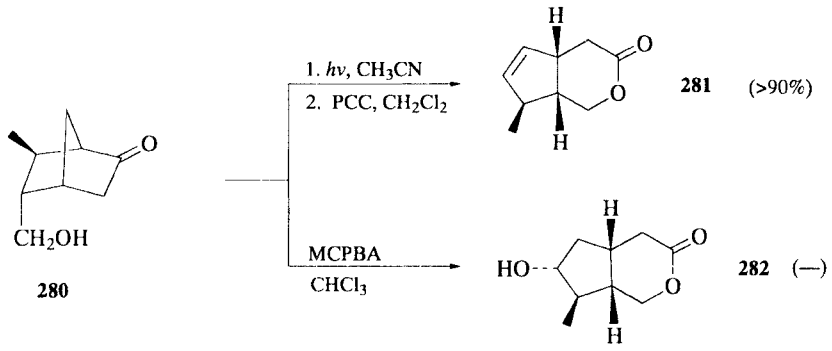
276 **277** (—)

from several 3-oxacyclopentanones and 3-oxacyclohexanones and some bicyclo[2.2.1]heptanon-2-ones.[724] An example of the latter is the rearrangement of bridged ketone **278** to give the lactol **279**.[350] Norrish type I reaction of bridged

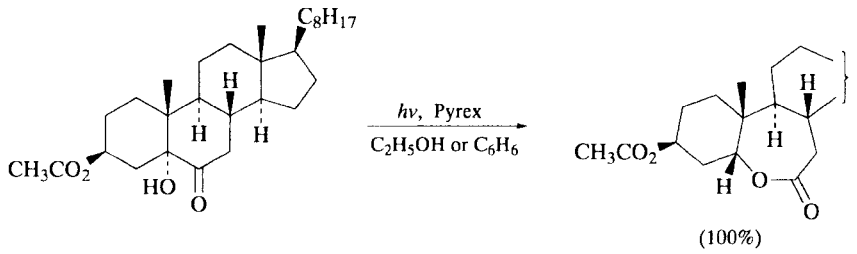


278 **279** (65%)

ketone **280** followed by oxidation is an alternative to Baeyer–Villiger reaction for the synthesis of the structurally similar lactones **281** and **282**.[355] Although other sim-

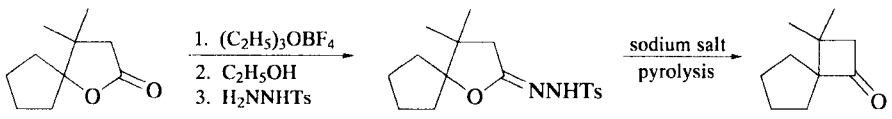


ple cyclopentanones and cyclohexanones do not give lactones, irradiation of an α-hydroxy-6-ketosteroid can result in stereospecific rearrangement to a lactone (Eq. 82).[310]



(Eq. 82)

Mechanistically related to the photochemical ring expansion of ketones to hemiacetals is the thermal decomposition of lactone tosylhydrazones (Eq. 83). The reaction sequence from lactone **283** to ketone **284** is formally a retro Baeyer–Villiger oxidation.[729]



283 **284** (42%)

(Eq. 83)

EXPERIMENTAL CONSIDERATIONS

Reagents and Conditions

This section describes the preparation and handling of the most frequently used Baeyer–Villiger reagents. At the time of the earlier review of this reaction hydrogen peroxide, permono- and perdisulfuric acid, peracetic acid, perbenzoic acid, and monoperphthalic acid were commonly used as reagents.[2] Since then, two commonly used oxidants have been TFPAA (90%), a powerful oxidant customarily prepared as needed from 90% hydrogen peroxide, and *m*-chloroperbenzoic acid (85%), a stable solid also prepared from 90% hydrogen peroxide. Unfortunately, problems associated with the use and transportation of 90% hydrogen peroxide, which is highly explosive,[730,731] have eliminated the commercial availability of reagents based upon this oxidant. If necessary, 90% hydrogen peroxide can be prepared by concentration of 30% hydrogen peroxide,[732] or substitution of commercially available 70% hydrogen peroxide (FMC Peroxygen Chemicals Division, Philadelphia, PA) might be attempted. In the alternative, judicious use of the information in this review concerning peracid purification procedures, alternative oxidants, catalysts, and radical scavengers which allow use of higher temperatures, should mitigate the loss of commercial reagents based upon 90% hydrogen peroxide.

In all peroxide oxidations of new compounds the possibility of reactions occurring with explosive violence must be considered.[2] *When tetrahydropyranyl ether derivatives were treated with alkaline hydrogen peroxide or 40% peracetic acid followed by washing with 10% sodium sulfite solution, attempted distillation led to detonation without prior warning.*[733]

Among the factors that go into choosing a peracid is its reactivity. The oxidizing power of a peracid is related to the strength of the conjugate acid of its leaving group; so the reactivity order of some commonly used peracids is TFPAA > monopermaleic acid,[349] > mono-*o*-perphthalic acid,[349] > 3,5-dinitroperbenzoic acid,[734] > *p*-nitroperbenzoic acid[424] > MCPBA = performic acid,[349] > perbenzoic acid > peracetic acid ≫ hydrogen peroxide > *tert*-butyl peroxide.[7]

Trifluoroperacetic Acid (90%). TFPAA (90%) is prepared prior to use by adding trifluoroacetic anhydride or trifluoroacetic acid[735] to a suspension of 90% hydrogen peroxide in methylene chloride at 0°.[3,7,42] Oxidations usually are performed in methylene chloride in the presence of a suspension of disodium hydrogen phosphate buffer, which usually eliminates transesterification as a side reaction. An example of a reaction is known which proceeds faster in the presence of 1 equivalent of buffer than 2 or more equivalents;[79] another reaction has been found to proceed better if the surface of a Teflon or Pyrex flask was virgin and not etched.[731] Typical reaction temperatures range from 0° to reflux, and reaction times are from a few minutes to several hours. There is no loss of active oxygen by TFPAA (90%) after 24 hours at reflux.[735] The TFPAA solutions prepared from 30% hydrogen peroxide have been used effectively;[736] but reactions are slowed.[735]

Nitroperbenzoic Acids. Crystalline 3,5-dinitroperbenzoic acid is prepared from 90% hydrogen peroxide and 3,5-dinitrobenzoic acid in methanesulfonic

acid.[734] Oxidation of unreactive substrates can be performed by refluxing with this reactive oxidant in halogenated solvents for several hours in the presence of a radical scavenger, 4,4′-thiobis(6-*tert*-butyl-3-methylphenol). The reagent is comparable in strength to TFPAA (90%), except that no buffers are needed.[734]

p-Nitroperbenzoic Acid (PNPBA) is a commercially available (Aldrich) crystalline solid, which can be prepared from *p*-nitrobenzoic acid and 94% hydrogen peroxide.[737–739] Oxidations are performed in halogenated solvents in the presence of a buffer, such as sodium bicarbonate.[424] The problems in manufacture from concentrated hydrogen peroxide may eliminate this peracid from commerce.

***m*-Chloroperbenzoic Acid (85%).** Oxidations with commercially available MCPBA (85%) generally are performed in chlorinated solvents at room temperature for several hours to several days. Some MCPBA oxidations proceed rapidly and in high yields when mixed in the solid state or when stirred in the presence of water, even though the ketone and MCPBA may be substantially insoluble.[740,741] Oxidation can be effected at 55° in 1,2-dichloroethane if a radical scavenger, such as 2,4,6-tri(*tert*-butyl)phenol, is added.[446] Common buffers utilized include sodium hydrogen phosphate, sodium acetate, and sodium bicarbonate. Catalysis can be effected with either buffer[227] or acids; such as trifluoroacetic acid,[742] methanesulfonic acid,[431] sulfuric acid,[323] or Nafion-H (DuPont), a perfluorinated resin sulfonic acid.[323] MCPBA (99+%) can be prepared from lower strength peracid by washing with phosphate buffer of pH 7.5.[743] MCPBA is exceptionally stable and decomposes less than 1% after 1 year at room temperature.[743] Although widely used formerly, MCPBA (85%) is no longer commercially available. Weaker solutions of MCPBA are available from various vendors. (See monoperoxyphthalic acid, magnesium salt, below.)

Monopermaleic acid. MPMA (30%) can be prepared by dissolving maleic acid in dimethylformamide, adding 30% hydrogen peroxide and stirring at 25° for several hours.[349] A solution of MPMA (30%) in methylene chloride is prepared by reacting 30% hydrogen peroxide and acetic anhydride in methylene chloride and then adding maleic anhydride.[744] MPMA (90%) is prepared by adding finely crushed maleic anhydride to 90% hydrogen peroxide in methylene chloride at 0°.[44,52] Oxidations are performed in methylene chloride at 25° or at reflux for 1–12 hours. Reactions are nearly as fast as those with TFPAA and no buffer is required. Permaleic acid solutions decompose to the extent of 5% in 6 hours at ambient temperature.[44]

Monoperphthalic Acid. The preparation of this acid has been discussed in *Organic Reactions*;[2,349,745] a modified procedure involves stirring finely powdered phthalic anhydride with 30% hydrogen peroxide in ether for 24 hours at 25°.[746] A 10% solution of monoperphthalic acid in ether at 3° for 30 days successfully oxidized a hindered acyl group to acetate after MCPBA, perbenzoic acid, and peracetic acid failed.[747]

Monoperphthalic Acid Magnesium Salt. Although little has been reported on use of MMPP to perform Baeyer–Villiger oxidations, this peracid is touted as a

replacement for MCPBA (85%).[748] MMPP is a non-shock-sensitive crystalline solid, comparable in solid state stability to MCPBA, which contains about 80% of the pure oxidant as its hexahydrate. Baeyer–Villiger oxidations are performed in dimethylformamide or methanol–water at 20–30° for 4–16 hours.[748] The oxidation byproduct, magnesium phthalate, is water soluble.

Persulfuric Acid. Preparation of this acid has been discussed in *Organic Reactions*.[2] Oxidations can be carried out in aqueous solutions of persulfuric acid,[541,749,750] and in methanol–sulfuric acid mixtures.[41] A stable mixture of potassium peroxymonosulfate, potassium hydrogen sulfate, and potassium sulfate has been described.[574]

Performic Acid. Preparation of this acid has been discussed in *Organic Reactions*.[745] Oxidations can be performed by adding 30% hydrogen peroxide to a solution of the substrate in formic acid[349] or in a buffered mixture of formic acid in methylene chloride.[616]

Peracetic Acid. Details of the preparation and titration of this acid are given in *Organic Reactions*.[2,745] Solutions containing approximately 40% peracetic acid are commercially available (Aldrich). Solutions of peracetic acid can be prepared by adding 90% hydrogen peroxide to a mixture of sulfuric acid and acetic anhydride[751,752] or 30% hydrogen peroxide to 90% aqueous acetic acid.[237] Oxidations are customarily performed in glacial acetic acid in the presence of sodium acetate.[349,424,753] Solutions of peracetic acid in acetone or ethyl acetate are used.[754] In a non-Baeyer–Villiger process the oxidizing effectiveness of a mixture of 30% hydrogen peroxide, acetic anhydride, and sulfuric acid is comparable to that reported for 90% hydrogen peroxide in an acetic acid/sulfuric acid mixture.[755]

Perbenzoic Acid. Details of the preparation of this acid are given in *Organic Reactions*.[2,745] Reactions are normally performed in chloroform, methylene chloride, or carbon tetrachloride; *p*-toluenesulfonic acid is often used as an acid catalyst.[306]

Hydrogen Peroxide–Base Catalysis. Use of basic hydrogen peroxide in Baeyer–Villiger and Dakin oxidations has been discussed in *Organic Reactions*.[2] Typically 6% hydrogen peroxide and 2 N sodium hydroxide are heated at 40–60° with the aldehyde for 1–12 hours.[545,549] Baeyer–Villiger oxidations of cyclobutanones and bicyclo[2.2.1]hepten-2-ones are effected using a mixture of aqueous 30% hydrogen peroxide and 10% sodium hydroxide in methanol or methanol–tetrahydrofuran.[190,195,397,415]

Hydrogen Peroxide–Acid Catalysis. Sulfuric acid catalyzes oxidation of electron-rich benzaldehydes with 31% hydrogen peroxide in methanol to give phenols.[579,611] Nafion-H (DuPont), a resin sulfonic acid, catalyzes the Baeyer–Villiger oxidation of cyclopentanones and cyclohexanones with 30% hydrogen peroxide in

methylene chloride. Reactions are performed at reflux temperature for 1–36 hours.[323] Cyclobutanones react to give lactones with 30% hydrogen peroxide in the presence of 2,2,2-trifluoroethanol, acetic acid, potassium hydrogen sulfate–methanol, ethanol, or acetonitrile.[756]

Alkyl Hydroperoxides–Base Catalysis. Cyclobutanones can be selectively oxidized in the presence of olefins and larger rings with commercially available [Aldrich] *tert*-butyl hydroperoxide and 10% sodium hydroxide in tetrahydrofuran.[272] Simple aliphatic ketones are oxidized to esters with 90% hydrogen peroxide and boron trifluoride etherate at room temperature.[46] Triphenylmethyl hydroperoxide–sodium hydroxide and 10% sodium hydroxide have been used in a similar manner for chemoselective cyclobutanone oxidation.[249,250]

Silylated Peracids. Silylated forms of hydrogen peroxide and persulfuric acid can be prepared from hydrogen peroxide.[757] Triphenylsilyl hydroperoxide behaves similarly to peracids with ketones on contact with basic alumina.[758] Bis(trimethylsilyl) peroxide[521] reacts with ketones in methylene chloride under the influence of trimethylsilyl trifluoromethanesulfonate,[221] stannic chloride,[220] or boron trifluoride etherate as catalysts.[220,477] Olefins are not attacked.

Bis(trimethylsilyl) monoperoxysulfate is prepared from bis(trimethylsilyl) peroxide. Unlike persulfuric acid, the silylated reagent is soluble in nonprotic and nonpolar media such as methylene chloride.[36,47] The reagent has general scope; however, it attacks olefins, and lactones may hydrolyze.

Benzeneperoxyseleninic Acids. Benzeneperoxyseleninic acid is generated in situ upon adding 30–90% hydrogen peroxide to benzeneseleninic acid or diphenyldiselenide in methylene chloride, tetrahydrofuran, or chloroform.[222,578,600,628] A phosphate buffer has been used.[222] Reaction times vary from an hour to several days at 25–40°. The reagent prepared using 30% hydrogen peroxide has proven successful when 40% peracetic acid and 85% MCPBA have failed.[222] More powerful oxidants prepared from the corresponding diselenides or seleninic acids include *o*-nitrobenzeneperoxyseleninic acid and 2,4-dinitrobenzeneperoxyseleninic acid.[578,600,628] These oxidants are expecially efficient for conversion of aryl aldehydes and ketones into phenols,[578] and for oxidation of α,β-unsaturated aldehydes to vinyl formates.[600,628]

Sodium Perborate. Sodium perborate is a cheap, large-scale industrial chemical. It is used for the Baeyer–Villiger oxidation of diaryl, arylalkyl, and cyclic ketones in either trifluoroacetic acid or acetic acid/trifluoroacetic acid mixtures at temperatures of 25–60° for 4–8 hours.[114]

Resin-Bound Peracids. Polystyrene-bound phenylseleninic acid is readily prepared from polystyrene.[43] Oxidations are effected by stirring a slurry of the ketone in methylene chloride with the resin and 30% hydrogen peroxide. Less water-soluble ketones are unreactive and appreciably water-soluble products undergo hydrolysis. The polymer can be reused, but it is destroyed by forcing conditions.

Arsenated polystyrene resins catalyze diphasic and triphasic Baeyer–Villiger oxidations of ketones in methanol, dioxane, or chloroform with 30% or 90% hydrogen peroxide at 80°. In water-miscible solvents, medium-size cycloalkanones, steroidal ketones, and branched-chain aliphatic ketones are oxidized.[182] Advantages of the reusable resins are their ease of separation from the reaction, low or no protic or Lewis acid activity, and the low cost and convenience of hydrogen peroxide, which gives water as its byproduct.

Polystyrene carboxylic acids catalyze epoxidations.[759] There are no reports found of their use in Baeyer–Villiger oxidations.

Uncommon Oxidants. Sparsely used Baeyer–Villiger reagents which have no reported advantage over more commonly used oxidants include *o*-sulfoperbenzoic acid in aqueous acetone,[760] *p*-carbomethoxyperbenzoic acid in chloroform,[761] *N*-β,β,β-trichloroethoxycarbonylperoxycarbamic acid (30%) in methylene chloride,[102,230] and *N*-benzoylperoxycarbamic acid (92%) in tetrahydrofuran.[102] Molybdenum peroxo complexes stabilized by picolinato and pyridine-2,6-dicarboxylato ligands catalyze oxidation of cyclic ketones by 90% hydrogen peroxide, but yields are poor.[762,763] Permonophosphoric acid, prepared from 90% hydrogen peroxide and phosphorus pentoxide, oxidizes acetophenones.[28] Effective permonophosphoric oxidations can be performed using 70% hydrogen peroxide; advantages in cost and rate of Baeyer–Villiger rearrangements under easy to run conditions should result in increased use of this peracid as commercial oxidants based upon 90% hydrogen peroxide become unavailable. Inexpensive and commercially available sodium percarbonate in trifluoroacetic acid conveniently and under mild conditions oxidizes aryl and cycloalkyl ketones to esters.[763a]

The Apparatus

For most reactions it is convenient to use a three-necked, round-bottomed flask equipped with an appropriately sized mechanical stirrer, and, if necessary a thermometer and dropping funnel. In some cases a drying tube may cap the reflux condenser or a gas inlet tube may be used to introduce nitrogen[549] or argon.[764] If long reaction times are anticipated, reactions may be run in the dark to minimize decomposition of the peracid reagent.

The Workup Procedure

For reactions performed in organic solvents, unreacted peracids generally are decomposed by addition of solutions of sodium bisulfite, sodium thiosulfate, or sodium sulfite.[334,349,415,578] Washing may be continued until a negative starch–iodide test is observed.[445] Insoluble resins and acids formed by decomposition of peracids are removed by filtration. Soluble acids are removed by washing with 10% solutions of sodium bicarbonate or sodium carbonate. Peracids are also removed by washing with these base solutions.

For reactions performed in nonorganic solvents with water-soluble peracids or aqueous hydrogen peroxide, the product is filtered if water insoluble[541] or *taken up* in an organic solvent, which is then treated as usual.[272]

Selection of Reaction Conditions. There is no evidence that alternative methods of introducing reactants (normal or inverse addition) has an effect on the yield of the Baeyer–Villiger oxidation. For sluggish reactions, it is often advantageous to add additional aliquots of peracid at regular intervals. Use of a buffer, such as sodium acetate, disodium hydrogen phosphate, or sodium bicarbonate, or avoidance of strong acid catalysts will minimize ester exchange and hydrolysis of the esters or lactones. Weaker peracids, such as peracetic acid, generally are more regioselective than stronger peracids, such as MCPBA.[349,424] A search for analogies in the tabular survey may facilitate the choice of the appropriate experimental conditions.

EXPERIMENTAL PROCEDURES

(2*R*,3*S*,22*R*,23*R*)-2,3,22,23-Tetrahydroxy-*B*-homo-7a-oxa-5α-ergostan-7-one Tetraacetate (Regioselective Oxidation of a Fused-Ring Ketone with 30% Trifluoroperacetic Acid).[736] To a solution of trifluoroperacetic acid in dichloromethane prepared by adding trifluoroacetic anhydride (3.37 mL) to 30% aqueous hydrogen peroxide (0.6 mL) in dichloromethane (3.7 mL) at 0° was added (2*R*,3*S*,22*R*,23*R*)-2,3,22,23-tetrahydroxy-5α-ergostan-7-one tetraacetate (100 mg) in dichloromethane (2.5 mL) at 0°. The mixture was stirred at room temperature for 1 hour and then was poured into 2% potassium carbonate solution and extracted with dichloromethane. The extract was washed with water, dried, and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 50% hexane–ethyl acetate afforded 98 mg (96%) of product as a glass: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.26 (m, 3β-*H*; $W_{1/2}$ = 8 Hz), 5.22 (dd, *J* = 10.5 and 8.4 Hz, 23-*H*), 5.04 (dd, *J* = 7 and 5.4 Hz, 22-*H*), 4.86 (m, $W_{1/2}$ = 12 Hz, 2β-*H*), 4.18 (dd, *J* = 10.5 and 8.4 Hz, 8β-*H*), 2.72 (dd, *J* = 10 and 15 Hz, 6β-*H*), 2.08 (s, CH_3CO), 2.05 (s, CH_3CO), 2.03 (s, CH_3CO), 1.98 (s, CH_3CO), 1.08 (s, 19-CH_3), 0.66 (s, 18-CH_3).

(*endo*, *endo*)-2,5-Dimethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (90% Trifluoroperacetic Acid Oxidation of a Bridged-Ring Ketone).[447] Trifluoroperacetic acid, prepared by dropwise addition of trifluoroacetic anhydride (7.1 mL, 50 mmol) to a stirred, ice-cold solution of 90% hydrogen peroxide (0.96 mL, 40 mmol) in 10 mL of dichloromethane (dried over magnesium sulfate and distilled), was added dropwise to a stirred, ice-cold mixture of finely ground disodium hydrogen phosphate (17.0 g, 120 mmol) in 25 mL of dichloromethane containing (*endo*, *endo*)-*cis*-2,4,-dimethyl-3-keto-8-oxabicyclo[3.2.1]octane (2.95 g, 20 mmol). After the reaction mixture had become too viscous for effective stirring (at approximately half addition of the peracid), the cooling bath was removed and the exothermic reaction was continued. The mixture was stirred for 2 hours at room temperature and then brought slowly to reflux for 15 minutes. The cooled mixture was filtered and the solids were washed thoroughly with dichloromethane. The combined filtrates were washed with water, 3% aqueous sodium bicarbonate, and brine, dried over magnesium sulfate, and concentrated to give an oil which crystallized on standing. Recrystallization from petroleum ether (bp 30–60°) afforded 3.2 g (94%) of product

as colorless needles, mp 57–59°; IR (CCl_4) 1740 and 1180 cm^{-1}; ^1H NMR (CCl_4) δ 1.07 (d, J = 7 Hz, 3H), 1.23 (d, J = 7 Hz, 3H), 1.90 (m, 4H), 2.93 (q, J = 7 Hz, 1H), 4.08 (m, 2H), 4.64 (q, J = 7 Hz, 1H).

***cis*-3-Hydroxymethylcyclopentaneacetic Acid Lactone (Oxidation with 85% *m*-Chloroperbenzoic Acid).**[445] A mixture of bicyclo[3.2.1]octan-3-one (15 g, 0.121 mol), purified *m*-chloroperbenzoic acid (35 g, 0.49 mol),[743] and sodium bicarbonate (21 g, 0.25 mol) in 500 mL of chloroform (freed of ethanol by passing over basic alumina) was mechanically stirred in a sealed flask and in the dark for 1 week. During that time, the built-up pressure was periodically released. The mixture was filtered and the solids were washed well with chloroform. The combined filtrates were washed several times with small volumes of cold 10% sodium sulfite solution until it gave a negative test with starch–iodide paper (about 350 mL of the sulfite solution is required), then with cold sodium bicarbonate solution and dried over sodium sulfate. After the solvent was removed the remaining oil was chromatographed on a silica gel column (250 g) developed with a mixture of petroleum ether (bp 30–60°)–chloroform (4:1). Two components identified (IR and NMR) as *m*-chlorobenzoic acid [recrystallized from ether–petroleum ether (bp 30–60°), mp 156–157°] and starting material (purified by sublimation) were eluted first. The composition of the eluent was then changed to 1:1, and fractions containing the product lactone were pooled and concentrated, leaving an oil that on drying in vacuo became a waxy solid. Recrystallization from petroleum ether (bp 30–60°), including treatment with Norit, gave a total of 10.4 g (61%) of product, mp 125–129°; IR (KBr) 2980, 1725, 1460, 1420, 1390, 1340, 1320, 1260, 1215, 1160, 1090, 1040, 990, 970, 935, 875, 852, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.19 (d, J = 3 Hz, CH_2O), 3.1–2.2 (envelope), 2.2–1.4 (envelope).

7β,8β,-Dihydroxy-*O*-isopropylidene-*N*-carbomethoxy-3-oxa-9-azabicyclo-[4.2.1^{1,6}]nonan-4-one (A Difficult Oxidation Under Forcing Conditions Using 85% *m*-Chloroperbenzoic Acid and a Radical Scavenger).[446] To a solution of 6β,7β-dihydroxy-*O*-isopropylidene-*N*-carbomethoxytropan-3-one (2.52 g, 9.9 mmol) in 60 mL of 1,2-dichloroethane was added 85% *m*-chloroperbenzoic acid (5.0 g, 29 mmol) and 2,4,6-tri(*tert*-butyl)phenol (20 mg). This mixture was heated to 55° and followed by gas chromatography [Hewlett Packard 700 Laboratory Chromatograph, SE-30 Ultraphase (10% w/w) with Chromosorb W support in 6 feet × 1/8 inch column]. After 22 hours the starting material had disappeared and the solution was cooled to −15° for 30 minutes to precipitate out most of the *m*-chloroperbenzoic acid. The acid was removed by filtration, and the filtrate was washed successively with cold 10% sodium bisulfite (15 mL), cold 10% sodium bicarbonate (3 × 15 mL), and saturated salt solution (20 mL). The organic phase was dried over magnesium sulfate and evaporated off, leaving a partially solidified oil. This was dissolved in anhydrous ether and allowed to crystallize at −15°, mp 117–118°. More product was obtained by adding petroleum ether (30–60°) and cooling to give a total yield 1.6 g (60%) of product; IR (CCl_4) 3000, 2960, 1755 (lactone), 1725 (urethane), 1455, 1392, and 1382 (*gem*-dimethyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26

(s, 3H), 1.40 (s, 3H), 2.93 (m, 2H), 3.73, (s, 3H), 4.33 (bm, 4H), 4.53 (d, 1H), 4.86 (d, 1H); mass spectrum, m/z 271 (M^+), 256 ($M^+ - CH_3$), 240 ($M^+ - OCH_3$), 214, 179, 142.

Phenyl Acetate (Acid-Catalyzed Oxidation with *m*-Chloroperbenzoic Acid).[742] To a solution of acetophenone (120 mg, 1 mmol) in anhydrous dichloromethane (2 mL) was added in one portion technical (80–85%) *m*-chloroperbenzoic acid (449 mg, 2.6 mmol). The suspension was cooled to 0° and distilled trifluoroacetic acid (114 mg, 1 mmol) was added dropwise over 5 minutes. The reaction flask was protected from light and the mixture was allowed to warm to room temperature; the progress of the reaction was followed by silica gel TLC. After 8 hours the mixture was diluted with dichloromethane (2 mL) and washed once each with 10% aqueous sodium sulfite solution (2 mL), saturated aqueous potassium carbonate solution (2 mL), and water (2 mL); dried over magnesium sulfate; and concentrated in vacuo to give 102 mg of pure phenyl acetate (75%).

Benzyl Benzoate (Solid-State Oxidation with *m*-Chloroperbenzoic Acid).[740] A mixture of powdered benzyl phenyl ketone and 2 mol equivalents of powdered 85% *m*-chloroperbenzoic acid was ground with agate pestle and mortar. After 24 hours the excess of peroxy acid was decomposed with aqueous 20% sodium bisulfite and the product was taken up in ether. The solution was washed with aqueous 20% sodium bicarbonate and water, dried over sodium sulfate and evaporated. The crude product was chromatographed on silica gel (benzene–chloroform) to provide benzyl benzoate (97%). For comparison, the oxidation of benzyl phenyl ketone (1 g) with *m*-chloroperbenzoic acid in chloroform (50 mL) after 24 hours afforded benzyl benzoate (46%).

Isobutyl Acetate (Preparation and Use of 90% Permaleic Acid to Oxidize a Straight-Chain Ketone).[44] To an ice-cold stirred solution of 11.6 g (0.34 mol) of 90% hydrogen peroxide and 150 mL of methylene chloride was added in one batch 39.2 g (0.4 mol) of freshly crushed maleic anhydride. When the major portion of the maleic anhydride had reacted, the solution was heated to reflux and 20 g (0.2 mol) of methyl isobutyl ketone was added in an equal volume of methylene chloride. When the theoretical amount of peracid had disappeared, as determined by iodimetric titration of aliquots, the solution was cooled, and the maleic acid was removed by filtration. The filtrate was washed twice with 100 mL of 10% sodium carbonate solution, once with 100 mL of 10% sodium bisulfite solution, and once with 100 mL of a saturated sodium chloride solution, and dried over magnesium sulfate. Distillation through a short Vigreux column yielded after removal of solvent 16.7 g (72%) of isobutyl acetate, bp 115–116°, n^{25}_D 1.3908.

12-Hydroxydodecanoic Acid Lactone (Oxidation with 30% Permaleic Acid).[744] Dichloromethane (1.6 L) and acetic anhydride (1.25 L) were stirred in a 5-L flask fitted with a double-surface reflux condenser and an overhead stirrer and cooled externally (ice water) while 30% hydrogen peroxide (1 L) was added. After

1 hour maleic anhydride (1 kg) was added, the mixture was cooled and stirred for 1 hour, and then the cooling bath was removed, whereupon the temperature rose during 1.5 hours and the mixture began to reflux. External cooling was resumed when needed to moderate the reaction. When little more heat was evolved, cyclododecanone (250 g, 0.62 mol) was added; this did not greatly increase the rate of heating, and when spontaneous refluxing ceased a heating mantle was used to maintain the mixture at reflux for 15 hours. The mixture was then cooled and the separated maleic acid was filtered off. The filtrate was washed in turn with water (3 × 600 mL), an aqueous solution containing 10% each of potassium hydroxide and sodium sulfite (2 × 300 mL), and then water (600 mL); tests for peroxide were now negative. After being dried (sodium sulfate) the filtrate was evaporated to give the lactone (210.4 g, 77%).

6-*endo*-Benzyloxy-8-*anti*-methoxy-2-oxabicyclo[3.2.1]octan-3-one and 6-*endo*-Benzyloxy-8-*anti*-methoxy-3-oxabicyclo[3.2.1]octan-2-one (Oxidation with 90% Perphthalic Acid).[749] Phthalic anhydride (0.96 g, 6.5 mmol) was dissolved in dimethylformamide (1 mL) and methylene chloride (1 mL). Hydrogen peroxide (90% in water; 0.17 g) was added to the stirred solution at 40°. After 1 hour, 6-*endo*-benzyloxy-7-*anti*-methoxybicyclo[2.2.1]heptan-2-one (0.5 g, 2 mmol) in chloroform (10 mL) was added. After stirring for 9 hours at 40° the solution was filtered and the filtrate was washed with saturated sodium sulfite solution (10 mL), saturated sodium bicarbonate solution (10 mL), and water (4 × 5 mL). The aqueous washings were back-extracted with methylene chloride (2 × 10 mL) and the combined organic extracts were dried and evaporated to give 0.44 g (83%) of a 73:27 mixture of product lactones as an oil, bp 155° (0.001 mm); IR 1740, 952, 930 cm $^{-1}$; ^{1}H NMR ($CDCl_3$) of the bridgehead migrated 2-oxa-3-oxo-lactone δ 7.29 (s, C_6H_5), 4.50 (m, H-1), 4.44 (s, OCH_2Ph), 4.28 (m, H-6), 3.87 (br s, H-8), 3.28 (s, OCH_3), 3.50–2.25 (m, H-4-*exo*, H-4-*endo*, H-7-*exo*), 1.92 (dm, J = 15 Hz, H-7-*endo*); ^{13}C NMR ($CHCl_3$) δ 169.44 (s, C-3), 83.40 (d, C-8), 78.59 (d, C-1), 78.43 (d, C-6), 38.48 (d, C-5), 37.00 (t, C-4) 31.23 (t, C-7). The minor methylene migrated 3-oxa-2-oxo-lactone was identified by spectral data; ^{13}C NMR ($CHCl_3$) δ 173.33 (s, C-2), 81.19 (d, C-8), 76.90 (d, C-6), 66.40 (t, C-4), 45.14 (d, C-1), 41.59 (d, C-5), 33.33 (t, C-7).

Caprolactone (Oxidation with Magnesium Monoperphthalate).[748] Cyclohexanone (314 mg, 3.2 mmol) was added to a stirred solution of magnesium monoperphthalate (1.39 g, 3.6 mmol) in dimethylformamide (15 mL) at 20°. After 16 hours, the mixture was diluted with methylene chloride (50 mL) and aqueous 2 M hydrochloric acid (20 mL) was added. The organic phase was washed with a saturated aqueous solution of sodium bicarbonate and dried over magnesium sulfate. Evaporation of the solvent, after confirming the absence of peroxide, gave the lactone (208 mg, 57%).

Methyl 7-Hydroxyheptanoate (Oxidation with Persulfuric Acid).[41] To a stirred mixture of concentrated sulfuric acid (245 mL) and water (98 mL), potas-

sium persulfate (182 g) was added at 10°. With the temperature kept below 5°, methanol (365 mL) and then methyl 8-oxo-nonanoate (100 g, 0.537 mol) was added. After stirring at 5° for 3 hours, the mixture was poured into saturated ammonium sulfate solution (1000 mL) and extracted with ethyl acetate (3 × 500 mL). The organic layers were collected, washed with saturated sodium thiosulfate (200 mL), 5% sodium bicarbonate (2 × 50 mL), and brine (2 × 50 mL), dried with sodium sulfate, and evaporated. Product (80 g, 93%) was obtained as an oily residue, pure according to TLC (silica gel; 6:4 hexane/ethyl acetate), bp 121–123° (1.5 mm); IR (neat) 3450 (broad), 1740 (C = O), 1430 cm^{-1}.

2-Oxo-2,5-dihydrofuran [2(5*H*)-furanone] (Oxidation of an Aryl Aldehyde with 30% Performic Acid).[616] A 1-L two-necked flask, equipped with an effective reflux condenser and a dropping funnel, was charged with furfural (practical grade; 96 g, 1 mol), dichloromethane (500 mL), formic acid (92.1 g, 2 mol), sodium sulfate (100 g), and potassium carbonate (35 g). This mixture was vigorously stirred and 30% hydrogen peroxide (75 mL) was added in one portion (exothermic reaction). Vigorous stirring was continued for 30–45 minutes after which time the mixture refluxed gently. Then, 30% hydrogen peroxide (125 mL) was added dropwise with continued stirring over a 3-hour period. The mixture was allowed to cool to room temperature (10 hours) with still continued stirring. The phases, which separated at once when stirring was stopped, were isolated and the inorganic phase was extracted with dichloromethane (1 × 100 mL). The organic phases were combined and the solvent was removed on a rotary evaporator. Then toluene (200 mL) was added and formic acid was removed by azeotropic distillation. To the residue, toluene (200 mL) was added, followed by the addition of triethylamine (1–2 g), and the flask was allowed to stand for 1 hour. Toluene was evaporated and the residual liquid was distilled in vacuo over a 30-cm Vigreux column to give, after a small forerun of furfural, 43–45 g of 99% pure (GLC) product (50–54%), bp 95–96° (19 mm), 79–81° (9 mm); ^1H NMR ($CDCl_3$) δ 4.91 (dd, J = 2.2 Hz, 1.7 Hz, 2H), 6.18 (dt, J = 2.2 Hz, 5.8 Hz, 1H), 7.58 (dt, J = 1.7 Hz, 5.8 Hz, 1H).

2′-Hydroxybiphenyl-2-carboxylic Acid Lactone (Oxidation with 90% Hydrogen Peroxide/Acetic Anhydride).[751] To a solution of 135 g of concentrated sulfuric acid and 350 g of acetic anhydride there was slowly added with stirring and cooling 55 mL of 90% hydrogen peroxide. The temperature was maintained below 15°. To this mixture a solution of 100 g (0.56 mol) of 9-fluorenone in 100 mL of methylene chloride was added and stirring was continued for 24 hours at −5°. Addition of 500 mL of water and subsequent boiling for 1–2 hours destroyed excess acetic anhydride and peroxides and removed the methylene chloride. The solid which precipitated on cooling was collected and dissolved in the combined ethereal extracts (3 × 100 mL) from the supernatant aqueous phase. The ethereal solution was washed with 5% sodium carbonate, then brine, and finally dried over sodium sulfate. Evaporation of the solvent (steam bath or flash evaporator) yielded 96 g (89%) of crude lactone, mp 87–89.5°. Two recrystallizations from ethanol (with Norit) afforded 86.2 g (80%) of fine white crystalline needles, mp 93–94°.

6-*endo*-Benzyloxy-8-*anti*-methoxy-2-oxabicyclo[3.2.1]octan-3-one (Oxidation with 30% Hydrogen Peroxide/Acetic Acid).[349] To a solution of 5-*endo*-benzyloxy-7-*anti*-methoxybicyclo[2.2.1]octan-2-one (24.6 g, 0.1 mol) in 90% aqueous acetic acid (100 mL) containing sodium acetate (8.2 g, 0.1 mol) there was added 30% hydrogen peroxide (110 mL, 1 mol). After stirring for 30 hours at 50°, sodium sulfite (252 g, 2 mol) was added followed by water (200 mL). The aqueous solution was extracted with chloroform (4 × 100 mL) and the chloroform extracts were washed with water (3 × 100 mL) and saturated sodium bicarbonate solution (150 mL). The aqueous extracts were back-extracted with chloroform (2 × 100 mL) and the combined organic fractions were dried over magnesium sulfate and evaporated to give 18.3 g (70%) of product as an oil, bp 155° (0.001 mm); IR 1740, 952, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (s, C_6H_5), 4.50 (m, H-1), 4.44 (s, OCH_2Ph), 4.28 (m, H-6), 3.87 (br s, H-8), 3.28 (s, OCH_3), 3.50–2.25 (m, H-4-*exo*, H-4-*endo*, H-7-*exo*), 1.92 (dm, J = 15 Hz, H-7-*endo*); ^{13}C NMR ($CHCl_3$) δ 169.44 (s, C-3), 83.40 (d, C-8), 78.59 (d, C-1), 78.43 (d, C-6), 38.48 (d, C-5), 37.00 (t, C-4), 31.23 (t, C-7).

6-(Benzyloxycarbonyl)-2-oxa-3-oxo-6-azabicyclo[3.2.2]nonane (Regioselective Oxidation with Commercial Peracetic Acid).[424] To *N*-benzyloxycarbonyl-2-azabicyclo[2.2.2]octan-5-one (400 mg, 1.53 mmol) in 1.5 mL of acetic acid containing 0.15 g of sodium acetate was added 1.5 mL of 28% peracetic acid. After the mixture was stirred in the dark for 18 hours, 15 mL of methylene chloride was added, the solution was washed with saturated aqueous sodium sulfite (4 × 5 mL) followed by saturated aqueous sodium bicarbonate (2 × 5 mL) and dried over magnesium sulfate. Removal of solvent in vacuo afforded 338 mg (80%) of lactone; bp 145–150° (0.025 torr); ^1H NMR ($CDCl_3$) δ 7.3 (s, 5H), 5.15 (s, 2H), 4.58 (br, H-1), 4.48 (br, H-5), 4.00 (dt, J = 13, 2 Hz, H-7n), 3.55 (dd, J = 13, 4 Hz, H-7x), 3.15 (dt, J = 17, 2 Hz, H-4), 2.3–1.8 (br, 4H).

(1*S,2*R**)-*exo*-3-Phenylselenyl-*cis*-bicyclo[3.3.0]oct-7-ene-2-spiro-4′-γ-butyrolactone (Regioselective and Chemoselective Cyclobutanone Oxidation with Basic Hydrogen Peroxide).**[195] A cooled (0°) basic hydrogen peroxide solution (30% aqueous hydrogen peroxide, 10.6 mL, 100 mmol; 10% aqueous sodium hydroxide, 15.1 mL) was added to 3.17 g (10.0 mmol) of (1*S**,2*R**)-*exo*-3-phenylselenyl-*cis*-bicyclo[3.3.0]oct-7-ene-2-spiro(2′-oxocyclobutane) in 70 mL of tetrahydrofuran and 35 mL of methanol at 0°. After 30 minutes, the reaction was quenched with reduction of the selenoxide by addition of an aqueous solution of sodium sulfite (35 g in 100 mL of water) and stirring for 5 minutes. The mixture was poured into a rapidly stirring mixture of 50 mL of dichloromethane and 100 mL of saturated aqueous sodium hydrogen sulfate. After 30 minutes, the organic phase was separated and the aqueous layer was extracted with 100 mL of dichloromethane followed by 2 × 100 mL of ethyl acetate. The combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuo to give an orange oil which was dissolved in about 20 mL of benzene containing a small amount of *p*-toluene-

sulfonic acid. The subsequent removal of the solvent in vacuo effected a dehydration to give the lactone. Purification by flash chromatography (500 mL hexanes; 1 L ether/hexanes, 1:3, 1 L ether/hexanes, 1:2, 100-mL fractions) gave 2.3 g (70%) of a white crystalline solid, mp 110–114°, R_f 0.58 (ether); IR ($CHCl_3$) 3080, 3060, 3010, 2960, 2920, 2860, 1770, 1580, 1475, 1450, 1435, 1280, 1230, 1200, 1160, 1060, 1040, 1020, 990, 960, 950, 925 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.26 (m, 3H), 5.84 (m, 1H), 5.50 (m, 1H), 3.30 (m, 1H), 3.23 (dd, J = 12.5 Hz, 1H), 3.0–1.85 (m, 8H); ^{13}C NMR (15 MHz, $CDCl_3$) δ 175.4, 134.4, 132.9, 128.7, 128.5, 127.0, 126.8, 94.9, 60.0, 51.0, 41.7, 41.1, 36.9, 29.1, 26.5.

Pyrogallol 1-Monomethyl Ether (Dakin Oxidation of a Phenolic Aldehyde Using Basic Hydrogen Peroxide).[549] The apparatus consisted of a 1-L three-necked flask fitted with a gas inlet tube extending about 3 cm into the flask and connected to the flask through a bubbler, a thermometer extending to the bottom, a mechanical stirrer, and a reflux condenser connected at the upper end with an exit tube leading to the hood. The reaction was carried out in an atmosphere of nitrogen or illuminating gas at the rate of 3 bubbles per second. In the flask were placed 60.8 g (0.4 mol) of 2-hydroxy-3-methoxybenzaldehyde and 200 mL of 2 N sodium hydroxide (0.4 mol). The mixture was stirred until almost all the solid had dissolved. The stirrer was replaced by a dropping funnel which contained 284 mL (0.5 mol) of 6% hydrogen peroxide (prepared by diluting 63 g of a solution containing 27% hydrogen peroxide with water to 284 mL). With occasional shaking, the hydrogen peroxide was added in portions of 20–25 mL. About 1 hour was required for the addition; the temperature was kept between 40 and 50°. After the addition of the first portion of hydrogen peroxide, the temperature rose to about 45° and a dark solution resulted. The temperature was allowed to fall to 40° before the next portion of the peroxide was added. After all the hydrogen peroxide was added, the reaction mixture was allowed to cool to room temperature and was then saturated with sodium chloride, after which it was extracted four times with 100-mL portions of ether. The combined extracts were dried over sodium sulfate. The ether was removed by distillation on a steam bath, and the residue was then distilled under reduced pressure. Pyrogallol monomethyl ether was collected at 136–138° (22 mm). The yield was 38–44.5 g (68–80%) of a colorless to light-yellow oil which solidified on standing.

4-Oxahomoadamantan-5-one (Nafion-H Acid Catalysis of 30% Hydrogen Peroxide Oxidation).[323] A mixture of adamantone (750 mg, 5 mmol) and the perfluorinated resinsulfonic acid Nafion-H (DuPont Company registered trademark, 250 mg) in dichloromethane (15 mL) was mixed with commercial 30% hydrogen peroxide (7.5 mL, 66 mmol) and stirred under reflux for 12 hours. The reaction mixture was filtered and the filtrate was extracted with dichloromethane followed by washing once with aqueous sodium bicarbonate and brine. Evaporation of solvent and direct sublimation gave glistening white crystals (798 mg, 96%) of product, mp 286–288°.

[3aα,5(S*),7aα]-3a,4,7,7a-Tetrahydro-6-methyl-5-[1-methyl-4-(tetrahydro-2H-pyran-2-yl)oxy]butyl-2-(3H)-benzofuranone (Regioselective and Chemoselective Oxidation of a Cyclobutanone with Basic *tert*-Butyl Hydroperoxide).[272] A mixture of 66 mg (0.22 mmol) of [1α,3(S*),6α]-4-methyl-3-[1-methyl-4-[(tetrahydro-2H-pyran-2-yl)oxybutyl]bicyclo[4.2.0]oct-3-en-7-one, 65 μL (0.66 mmol) of *tert*-butyl hydroperoxide, and 103 μL (0.26 mmol) of 10% aqueous sodium hydroxide in 2.3 mL of tetrahydrofuran cooled to 0° was stirred for 30 minutes. The reaction mixture was taken up in 50 mL of benzene–ether (1:1) and was washed with 2 mL of water and two 2-mL portions of brine. The organic layer was dried over magnesium sulfate and the solvent was evaporated in vacuo leaving 60 mg of crude lactone. Purification with 5 g of silica gel (elution with ether–benzene, 2:3) afforded 53 mg (76%) of pure product as an oil; IR (CCl_4) 2955, 2945, 2880, 1784, 1555, 1455, 1445, 1422, 1390, 1359, 1350, 1330, 1290, 1255, 1220, 1210, 1190, 1145, 1124, 1085, 1039, 998, 990, 940, 915, 868 cm^{-1}; ^1H NMR (CCl_4) δ 4.68 (m, 1H), 4.53 (br s, 1H), 1.78 (s, 3H), 0.95 (d, J = 7 Hz, 3H).

5,5,9-Trimethyl-10-oxatricyclo[7.3.2.0^{1,6}]tetradec-6-en-11-one (Chemoselective and Regioselective Oxidation of a Bridged Ketone Using bis(Trimethylsilyl) Peroxide).[477] To a solution of 5,5,9-trimethyltricyclo[7.2.2.0^{1,6}]tridec-6-en-10-one (120.2 mg, 0.517 mmol) and bis(trimethylsilyl) peroxide[521] (440 mg, 2.59 mmol) in methylene chloride (5 mL) was added boron trifluoride etherate (0.320 mL, 2.59 mmol) at −20°. After stirring 1 hour at −20 to −10°, the reaction was quenched with 5% aqueous sodium thiosulfate. The mixture was allowed to warm to room temperature and extracted with two portions of ether. The extracts were combined, washed with saturated sodium bicarbonate solution and saturated brine, dried over magnesium sulfate, and concentrated in vacuo. Chromatography (6 g of silica gel: 10:1 hexane–ethyl acetate) of the remaining oil (142.8 mg) gave 54.9 mg (43%) of product as colorless needles, mp 106–107°; IR (CCl_4) 1720 cm^{-1}; ^1H NMR (CCl_4) δ 5.50 (dd, J = 5.7 Hz, 4.1 Hz, 1H), 2.98 (br d, J = 16.2 Hz, $W_{1/2}$ = 3 Hz, 1H), 2.49 (d, J = 16.2 Hz, 1H), 2.5–1.2 (m, 12H), 1.32 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H); mass spectrum (13.4 eV) m/z (rel intensity) 248 (M^+, 100), 233 (3.9), 206 (83.2), 189 (43.9), 188 (58.5), 179 (26.7), 177 (80.2), 166 (46.2), 82 (10.2).

Tetraphenyl-α-pyrone [Preparation and Use of bis(Trimethylsilyl) Monoperoxysulfate, a bis(Trimethylsilyl)-Buffered Reagent with Advantages over Caro's Acid].[47] A 100-mL, three-necked, round-bottom flask, equipped with a pressure-equalizing addition funnel, Teflon spinbar, rubber septum cap, and a three-way stopcock, was attached to a nitrogen manifold. Under a nitrogen atmosphere, a solution of 1.0 g (5.6 mmol) of bis(trimethylsilyl) peroxide in 20 mL of dry methylene chloride was syringed into the reaction vessel. After the mixture was cooled to −30° with stirring, 25 mL of a 0.2 M solution of sulfur trioxide in methylene chloride was added dropwise from the addition funnel over a period of 15 minutes, carefully maintaining the reaction mixture at −30°. The reaction progress was

monitored by ^{1}H NMR, observing the appearance of the trimethylsilyl product signal as a singlet at δ 0.40. After completion of the reaction (about 30 minutes), this solution was added to 526 mg (1.4 mmol) of tetracyclone in 10 mL of dry methylene chloride at −30° over 45 minutes. The reaction mixture was allowed to warm to room temperature (about 30°) and kept at this temperature for 8 hours. To the mixture was added 5 mL of water, the solution was transferred to a separatory funnel, the aqueous layer was siphoned off, and the methylene chloride layer was washed with 2 × 20 mL of 5% aqueous sodium bicarbonate and dried over magnesium sulfate. Rotoevaporation of the solvent and purification of the crude product by silica gel chromatography gave 417 mg (76%) of tetraphenyl-α-pyrone, IR and ^{1}H NMR identical with authentic material.

Phenylacetaldehyde (Regioselective Oxidation of an α,β-Unsaturated Aldehyde with 30% Hydrogen Peroxide Catalyzed by 2-Nitrophenylbenzeneperseleninic Acid).[628] To a vigorously stirred solution of cinnamaldehyde (13.2 g, 0.1 mol) in dichloromethane (100 mL), bis(2-nitrophenyl) diselenide (1.5 g, 3.7 mmol) and 30% hydrogen peroxide (25 mL, 0.22 mol) were added. The mixture was stirred at room temperature until all aldehyde was consumed (TLC). The solid was filtered off and washed with dichloromethane and water. The filtrate was transferred to a separatory funnel and the layers were separated. The organic layer was washed with water, 5% aqueous sodium bicarbonate, 10% aqueous sodium bisulfite, again with water, and then dried over sodium sulfate. The solvent was evaporated in vacuo, the residue was dissolved in ether (100 mL), water (100 mL) and sodium bicarbonate (10 g, 0.12 mol) were added, and the mixture was vigorously stirred at room temperature for 31 hours. The organic layer was separated, washed with water, and dried over sodium sulfate. Ether was evaporated and phenylacetaldehyde was distilled at reduced pressure, bp 92° (20 mm), yield 7.5 g (63%), 2,4-dinitrophenylhydrazone mp 121°.

Phenyl Benzoate (A General Procedure for Use of Sodium Perborate, an Inexpensive Oxidant).[114] A mixture of 4.98 g (3 mol) of sodium perborate tetrahydrate and 1.82 g (0.01 mol) of benzophenone in 30 mL of trifluoroacetic acid was stirred for 4–8 hours. The inorganic salts were removed by filtration, and ice water (about 250 mL) was added. The crude product could be isolated following extraction with methylene chloride as described previously to afford 1.60 g (81%) of product identical with known material.[42,734]

TABULAR SURVEY

The information in the following tables is an extension of examples of the Baeyer–Villiger reaction of ketones and aldehydes with peracids reviewed previously and covers the literature from January, 1954 through December, 1989. Significant reactions reported in 1990–91 are also included. The arrangement of the tables follows that used in the previous review[2] with several exceptions. The table on oxidation of alicyclic ketones has been expanded to three tables to accommodate

examples of monocyclic and spirocyclic, fused bicyclic and polycyclic, and bridged bicyclic and polycyclic substrates. The table on polycarbonyl compounds includes only 1,2-dicarbonyl compounds; otherwise the structure is treated as a monocarbonyl compound. New tables on α,β-unsaturated aldehydes, ketals and acetals, and nitrogen derivatives of ketones and aldehydes have been added. The separate table for aromatic ketones has been removed and they are now listed in the appropriate sections. The tables include examples of oxidations of carbonyl compounds under Baeyer–Villiger conditions that have led to formation of products other than esters or lactones. Because hydrogen peroxide and several metal oxidants also react with ketones to afford lactones, such reactions are often considered in the current literature to be Baeyer–Villiger reactions. The tables also include examples of such Baeyer–Villiger-like oxidations because of their utility in synthesis and similarity in mechanism.

The carbonyl compounds in the tables are arranged according to total carbon content in the molecular formula of the starting ketone. Ketals and acetals are arranged according to carbon content of the parent ketone. Within each category based on carbon content, the compounds are arranged by complexity of molecular formula according to the *Chemical Abstracts* convention. When molecular formulas are identical, structures are arranged from the simpler to the more complex and from the smaller ring sizes to the larger ones.

When multiple references are cited for an entry, the conditions quoted provide the best product yield and are given in the first reference. The conditions stated refer in most cases only to the oxidation itself. Overnight reactions are reported as "12 h." Room temperature oxidations are reported as "25°." Product yields are in parentheses; the yield of recovered starting material is indicated by an asterisk. A dash means that the yield of product has not been reported. Subsequent references for an entry provide the same product, but may use the same or a different oxidant or an alternative set of conditions.

The following abbreviations are used in the tables:

Ac	acetyl
Bn	benzyl
BPC	*N*-benzoylperoxycarbonic acid
BTMSP	bis(trimethylsilyl) peroxide
CAN	ceric ammonium nitrate
diglyme	diethylene glycol dimethyl ether
3,5-DNPBA	3,5-dinitroperbenzoic acid
ether	diethyl ether
HMPA	hexamethylphosphoric triamide
LDA	lithium diisopropylamide
MCPBA	*m*-chloroperbenzoic acid (chloroform is always present unless otherwise stated)
MPPA	monoperphthalic acid
Nafion	a poly(perfluorosulfonic acid) (DuPont Trademark)

PAA	peracetic acid (acetic acid is always present)
PBA	perbenzoic acid (chloroform is always present unless otherwise stated)
PMA	monopermaleic acid
pNBn	*p*-nitrobenzyl
pNPBA	*p*-nitroperbenzoic acid
PSA	persulfuric acid (sulfuric acid is always present)
TBMP	di(5-*tert*-butyl-4-hydroxy-2-methyl) sulfide
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TECTA	*N*-β,β,β-trichloroethoxycarbonyl-1,2,4-triazole
TFPAA (%)	trifluoroperacetic acid (percent hydrogen peroxide used in its preparation)
Ts	*p*-toluenesulfonyl

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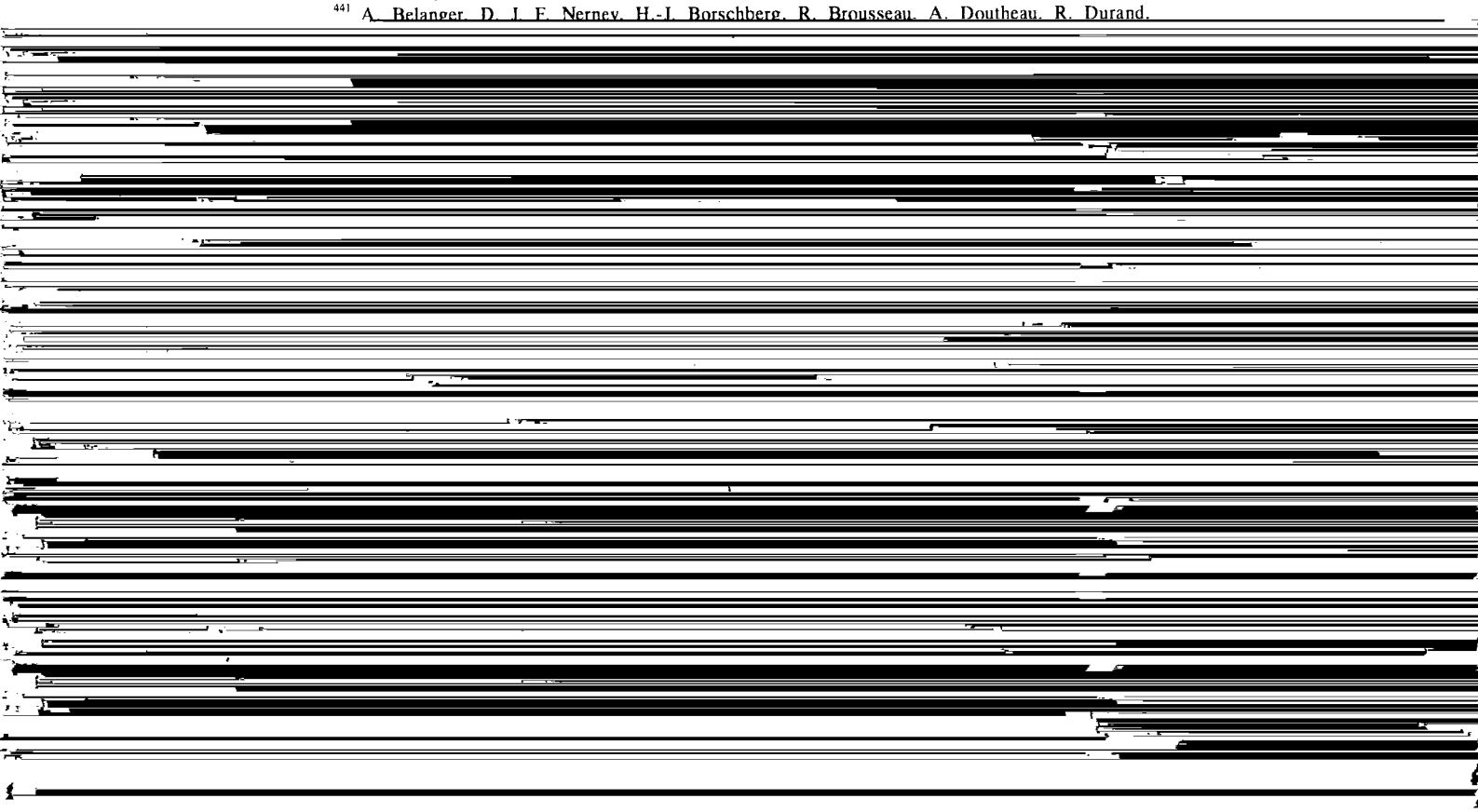

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