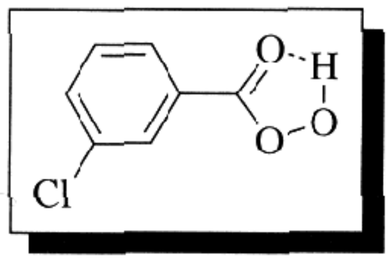
S. D. Burke & R.L. Danheiser,
Handbook of Reagents for Organic Synthesis
Oxidizing and Reducing Agents

m-Chloroperbenzoic Acid[1]



[937-14-4] $C_7H_5ClO_3$ (MW 172.57)

(electrophilic reagent capable of reacting with many functional groups; delivers oxygen to alkenes, sulfides, selenides, and amines)

Alternate Name: m-CPBA; MCPBA.

Physical Data: mp 92–94 °C.

Solubility: sol CH_2Cl_2, $CHCl_3$, 1,2-dichloroethane, ethyl acetate, benzene, and ether; slightly sol hexane; insol H_2O.

Form Supplied in: white powder, available with purity of 50%, 85%, and 98% (the rest is 3-chlorobenzoic acid and water).

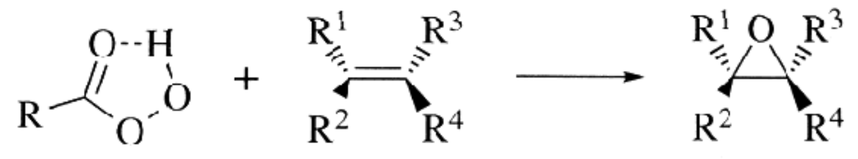
Analysis of Reagent Purity: iodometry.[2]

Purification: commercial material (purity 85%) is washed with a phosphate buffer of pH 7.5 and dried under reduced pressure to furnish reagent with purity >99%.[3]

Handling, Storage, and Precautions: pure *m*-CPBA is shock sensitive and can deflagrate;[4] potentially explosive, and care is required while carrying out the reactions and during workup.[5] Store in polyethylene containers under refrigeration.

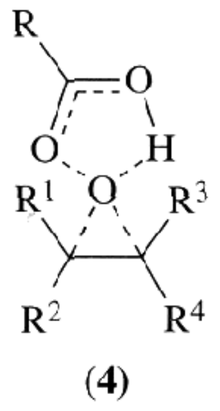
Functional Group Oxidations. The weak O–O bond of *m*-CPBA undergoes attack by electron-rich substrates such as simple alkenes, alkenes carrying a variety of functional groups (such as ethers, alcohols, esters, ketones, and amides which are inert to this reagent), some aromatic compounds,[6] sulfides, selenides, amines, and N-heterocycles; the result is that an oxygen atom is transferred to the substrate. Ketones and aldehydes undergo oxygen insertion reactions (Baeyer–Villiger oxidation).

Organic peroxy acids (**1**) readily epoxidize alkenes (eq 1).[1b] This reaction is *syn* stereospecific;[7] the groups (R^1 and R^3) which are *cis* related in the alkene (**2**) are *cis* in the epoxidation product (**3**). The reaction is believed to take place via the transition state (**4**).[8] The reaction rate is high if the group R in (**1**) is electron withdrawing, and the groups R^1, R^2, R^3, and R^4 in (**2**) are electron releasing.



(1)

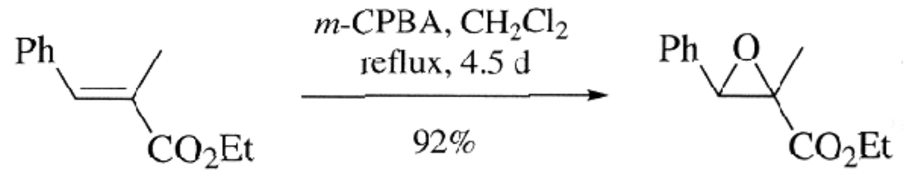
(**1**) (**2**) (**3**)



(**4**)

Epoxidations of alkenes with *m*-CPBA are usually carried out by mixing the reactants in CH_2Cl_2 or $CHCl_3$ at 0–25 °C.[9] After the reaction is complete the reaction mixture is cooled in an ice bath and the precipitated *m*-chlorobenzoic acid is removed by filtration. The organic layer is washed with sodium bisulfite solution, $NaHCO_3$ solution, and brine.[10] The organic layer is dried and concentrated under reduced pressure. Many epoxides have been purified chromatographically; however, some epoxides decompose during chromatography.[11] If distillation (*caution*: check for peroxides[12]) is employed to isolate volatile epoxides, a trace of alkali should be added to avoid acid-catalyzed rearrangement.

Alkenes having low reactivity (due to steric or electronic factors) can be epoxidized at high temperatures and by increasing the reaction time.[13] The weakly nucleophilic α,β-unsaturated ester (**5**) thus furnishes the epoxide (**6**) (eq 2).[13b] When alkenes are epoxidized at 90 °C, best results are obtained if radical inhibitor is added.[13a] For preparing acid-sensitive epoxides (benzyloxiranes, allyloxiranes) the pH of the reaction medium has to be controlled using $NaHCO_3$ (as solid or as aqueous solution),[14] Na_2HPO_4, or by using the *m*-CPBA–KF[9a] reagent.



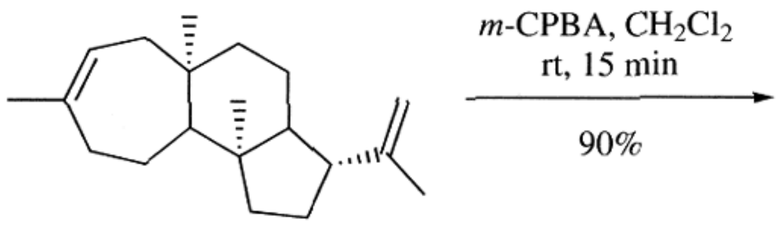
(2)

(**5**) (**6**)

Regioselective Epoxidations. In the epoxidation of simple alkenes (**2**) (eq 1), due to the electron-releasing effect of alkyl groups the reactivity rates are tetra- and trisubstituted alkenes > disubstituted alkenes > monosubstituted alkenes.[1a] High regioselectivity is observed in the epoxidation of diene hydrocarbons (e.g. **7**) having double bonds differing in degree of substitution (eq 3).[15] Epoxidation takes place selectively at the more electron-rich C-3–C-4 double bond in the dienes (**8**)[16] and (**9**).[17]

Diastereoselective Epoxidation of Cyclic Alkenes. π-Facial stereoselectivity (75% *anti*) is observed in the epoxidation of the allyl ether (**10a**) since reagent approach from the α-face is blocked by the allylic substituent; a higher diastereoselectivity (90% *anti*

epoxidation) is observed when the bulkier O-*t*-Bu is located on the allylic carbon (eq 4).[18] Due to steric and other factors, the norbornene (**11**) undergoes selective (99%) epoxidation from the *exo* face.[19] In 7,7-dimethylnorbornene (**12**), approach to the *exo* face is effectively blocked by the methyl substituent at C-7, and (**12**) is epoxidized from the unfavored *endo* face, although much more slowly (1% of the rate of epoxidation of **11**).[19] The geminal methyl group at C-7 is able to block the approach of the peroxy acid even when the double bond is exocyclic to the norbornane ring system (for example, epoxidation of (**13**) proceeds with 86% *exo* attack, while (**14**) is oxidized with 84% *endo* attack). Folded molecules are epoxidized selectively from the less hindered convex side; *m*-CPBA epoxidation of the triene lactone (**15**) takes place from the α-face with 97% stereoselectivity.[20] The triepoxide (**16**) has been obtained in 74% yield by epoxidizing the corresponding triene;[21] in the epoxidation step, six new chiral centers are introduced stereoselectively as a result of steric effects.



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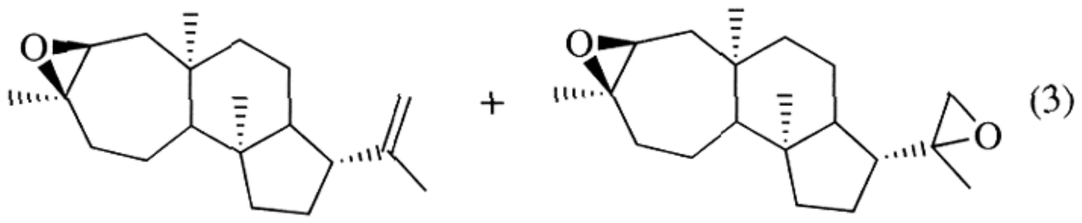
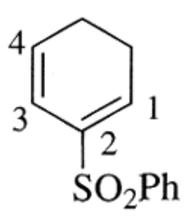


(3)

86% 4%



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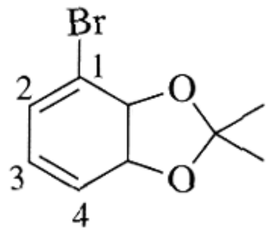

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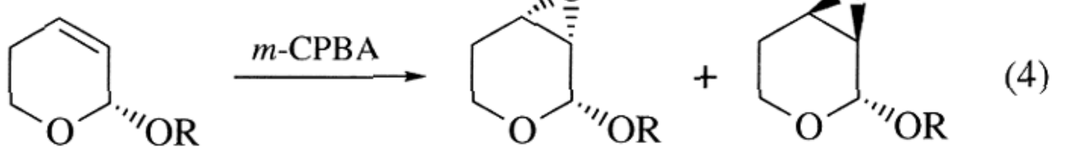
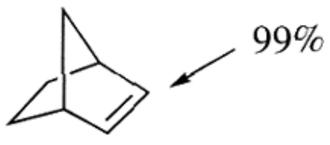


(4)

(10)

(**a**) R = Me 1:3

(**b**) R = *t*-Bu 1:9



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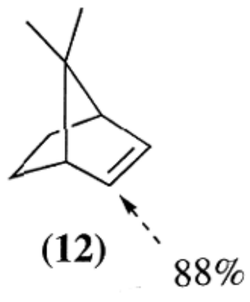

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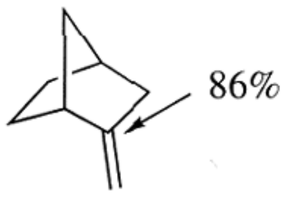

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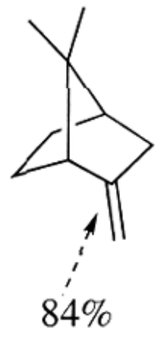

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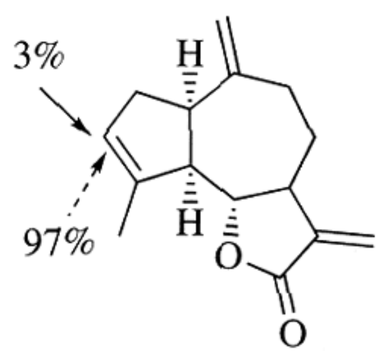

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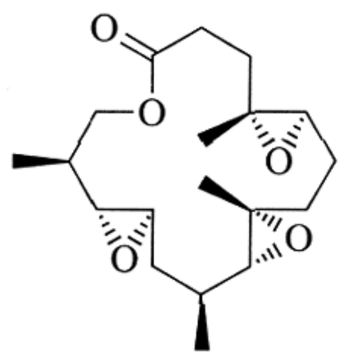
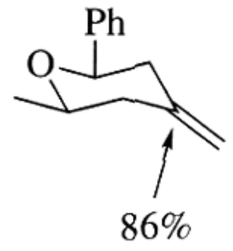


(16)

Unhindered methylenecyclohexanes and related compounds show a moderate preference for axial epoxidation. In the epoxidation of (**17**) the ratio of axial:equatorial attack is 86:14;[22] for the alkene (**18**) the ratio is 75:25.[23]



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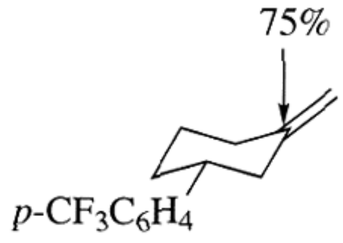
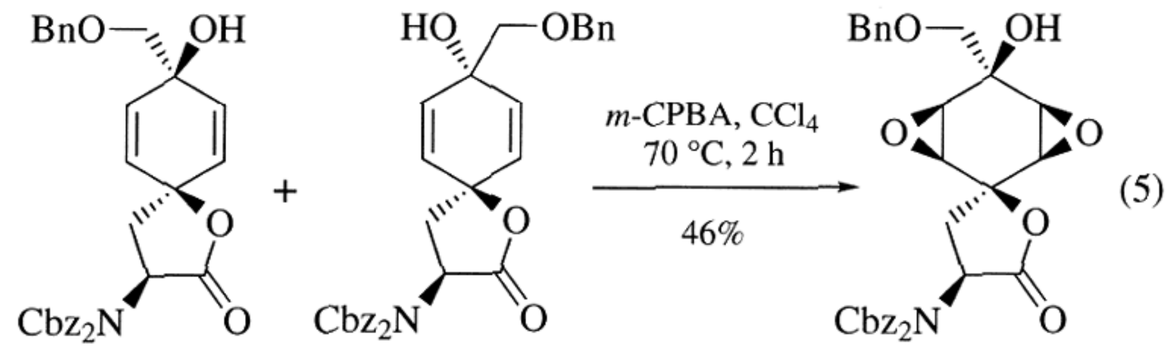


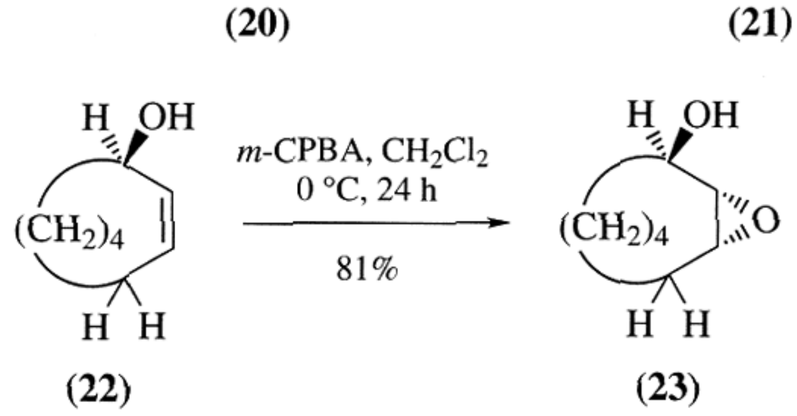
(18)

Epoxidation of Cyclic Alkenes having Directing Groups. Henbest showed that in the absence of severe steric interference, allylic cyclohexenols are epoxidized stereoselectively by organic peroxy acids to furnish *cis*-epoxy alcohols;[24a] a large number of *cis*-epoxy alcohols have been prepared by epoxidizing allylic cyclohexenols.[7] A mixture (5:1) of labile bisallylic alcohols (**19**) and (**20**) was reacted with *m*-CPBA (eq 5); from the reaction mixture diepoxide (**21**) was isolated as a single isomer.[25] Epoxidation of (*Z*)-cyclooct-2-en-1-ol (**22**) furnishes exclusively (99.8%) the *trans*-epoxide (**23**) (eq 6).[24b] Similar observations have been made subsequently.[26] This result, as well as the stereoselectivity observed during the epoxidation of other allylic alcohols, both cyclic and acylic, has been rationalized on the basis of transition state models.[24,27]



(5)

(19) (20) (21)



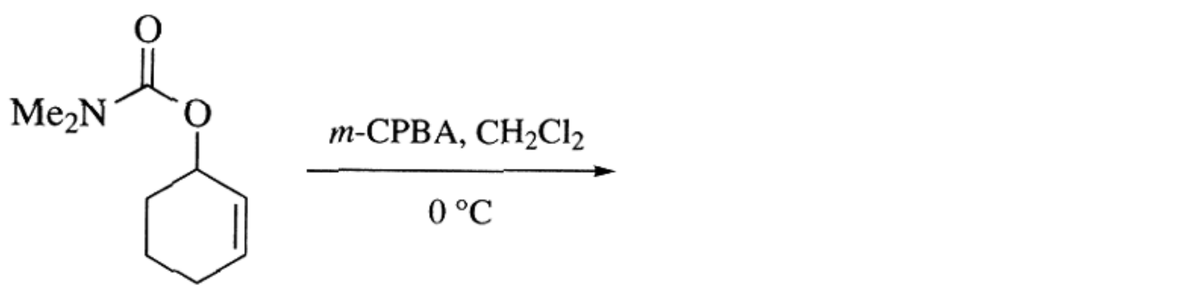
(6)

(22) (23)

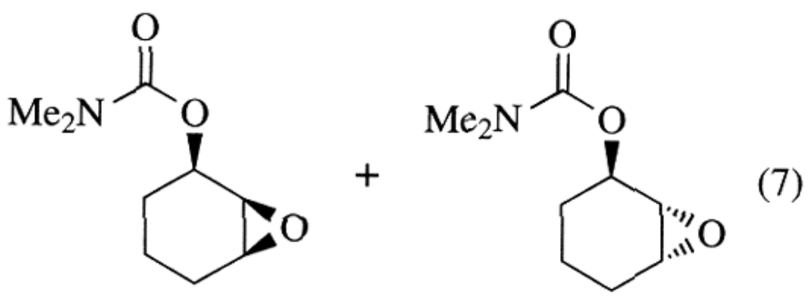
Stereoselectivity has been observed during the peroxy acid epoxidation of some homoallylic and bishomoallylic alcohols,[28] and the epoxidation of the allylic carbamate (**24**) is *syn* stereoselective (eq 7).[28]

Epoxidations of Acyclic Alkenes. Since acyclic systems normally are not rigid, high stereoselectivity has been observed only when special structural features are present. The presence of functional groups (OH, NH, CO, and ether) which form hydrogen bonds with the peroxy acid can facilitate stereoselective epoxi-

dations by imparting rigidity to the system. High *anti* selectivity (>95%) has been observed in the epoxidation of both (**25**) and (**26**) each of which has a branched substituent adjacent to the carbon carrying the silicon group.[29] High *anti* selectivities have been noted during the epoxidation of (**27**) (95%),[30] (**28**) (96%),[31] (**29**) (95%),[32] and (**30**) (96%).[33] High *syn* selectivity has been observed in the reactions of (**31**) (98%)[33] and (**32**) (93%).[34] When the allyl alcohol (**28**) reacts with *m*-CPBA, in the transition state the reagent is hydrogen-bonded to the ether oxygen as well as to allylic hydroxyl. The high selectivity is due to the cooperative effect of the hydroxyl group and the ether oxygen.[31]

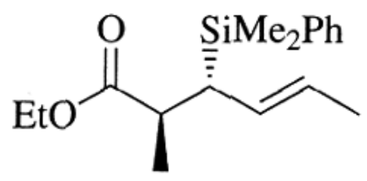


(**24**)

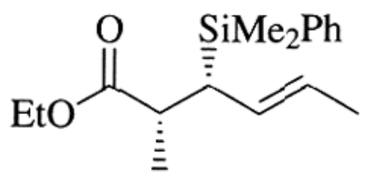


(7)

cis:*trans* = 10:1

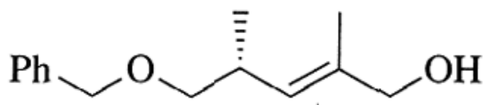


(**25**)

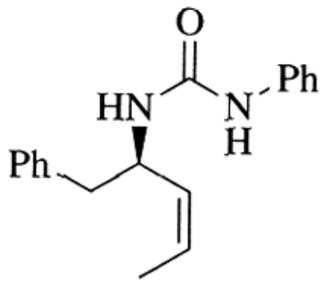


(**26**)

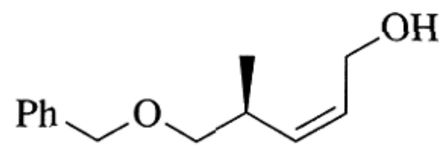
(**27**)



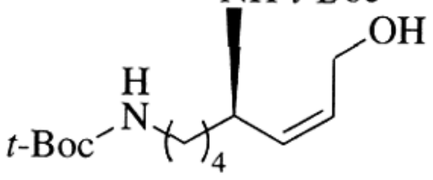
(**28**)



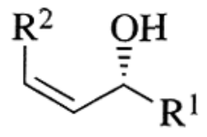
(**29**)



(**30**)



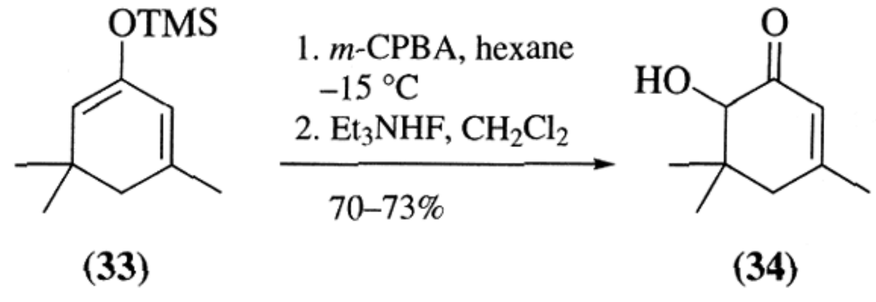
(**31**)



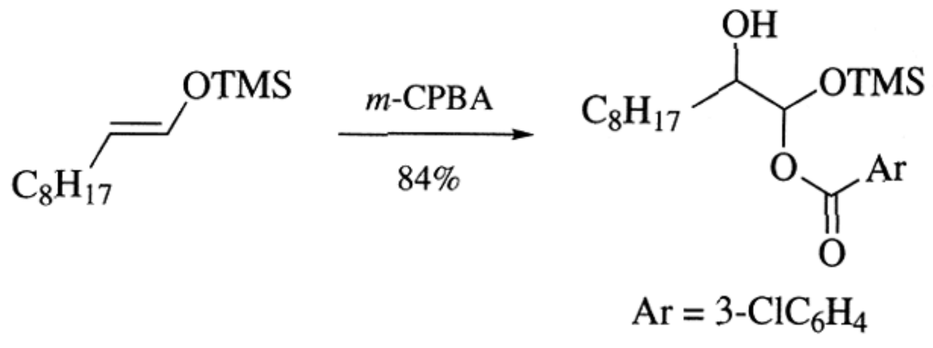
(**32**) $R^1 = (CH_2)_6CO_2Me$
$R^2 = (CH_2)_5Me$

High stereoselectivity has also been observed in the epoxidation of some acyclic homoallylic alcohols.[35]

Oxidation of Enol Silyl Ethers and Furans. Epoxides of enol silyl ethers undergo facile ring opening and only in rare cases have stable epoxides been isolated.[36] α-Hydroxy enones have been prepared in two steps from α,β-unsaturated ketones; the enol silyl ether (**33**) prepared from the corresponding enone is treated with *m*-CPBA and the resulting product reacts with triethylammonium fluoride to furnish an α-hydroxy enone (**34**) (eq 8).[37] This method has also been used for the preparation of α-hydroxy ketones,[38] α-hydroxy acids,[39] and α-hydroxy esters. As illustrated in (eq 9), aldehydes have been converted to protected α-hydroxy aldehydes in a similar fashion.[40] Epoxidation of enol silyl ethers according to eq 10 has been used in synthesizing α,α′-dihydroxy ketones from methyl secondary alkyl ketones; the silyl ether (**36**) furnishes the corresponding dihydroxy ketone quantitatively upon brief acidic treatment.[41] Peroxy acid oxidation of furfuryl alcohols yields pyranones according to eq 11.[42,43] Furfurylamides also react similarly.[44]



(**33**) (**34**) (8)



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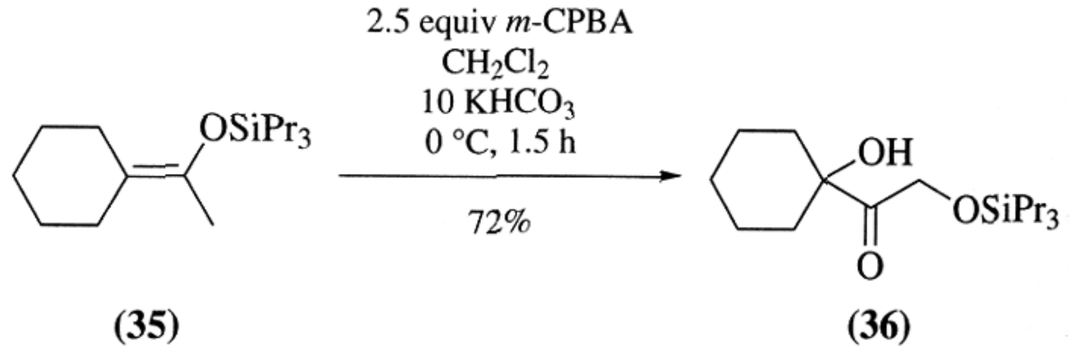
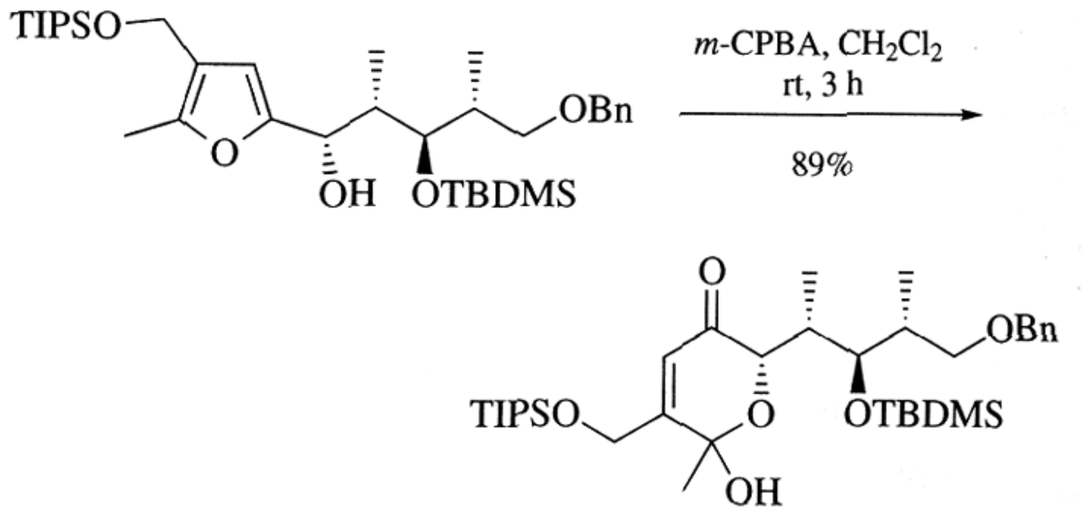
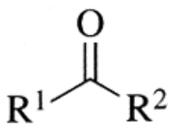


(**35**) (**36**) (10)



(11)

Baeyer–Villiger Rearrangement. Reaction of a ketone (**37**) with peroxy acid results in oxygen insertion to furnish the esters (**38**) and (**39**). This reaction, known as the Baeyer–Villiger rearrangement, has been reviewed recently.[45] Cyclobutanones undergo very facile rearrangement with peroxy acids, as well as with ***Hydrogen Peroxide*** in presence of base. The cyclobutanone (**40**) reacted readily with *m*-CPBA to furnish regio-, stereo-, and chemoselectively the lactone (**41**) (eq 12),[38b] which was elaborated to gingkolide. Baeyer–Villiger reaction of (**40**) with H_2O_2/base furnished a γ-lactone which was the regioisomer of (**41**). When 1,2,3,8,9,9a-hexahydro-1-methyl-3a,8-methano-3a*H*-cyclopentacycloocten-10-one, which has double bonds as well as a keto group, was treated with *m*-CPBA, exclusive alkene epoxidation was observed.[46] Ketones having stannyl groups on the β-carbon undergo a tin-directed Baeyer–Villiger reaction.[47]



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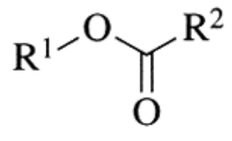

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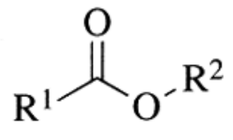

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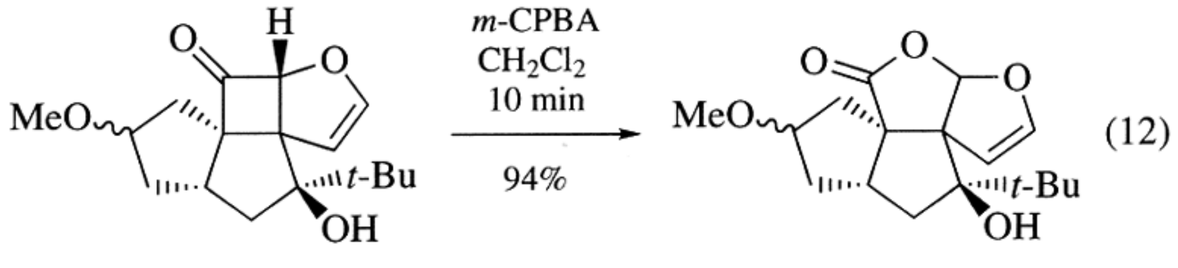
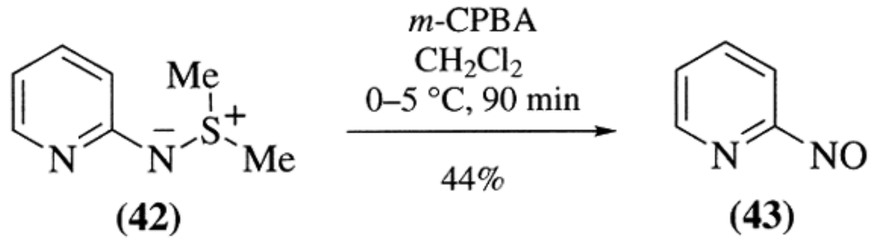


(40) (41) (12)

Oxidation of Nitrogen-Containing Compounds. Primary amines are oxidized by *m*-CPBA to the corresponding nitro compounds. One of the intermediates formed in this reaction is the corresponding nitroso compound, which reacts sluggishly with the reagent. High yields are obtained by carrying out the reaction at a high temperature (≈83 °C) and increasing the reaction time (3 hours). For example, *n*-hexylamine is oxidized to 1-nitrohexane in 66% yield.[48] When a substrate having the amino group at a chiral center was oxidized, the nitro compound was formed with substantial (≈95%) retention of configuration.[49]

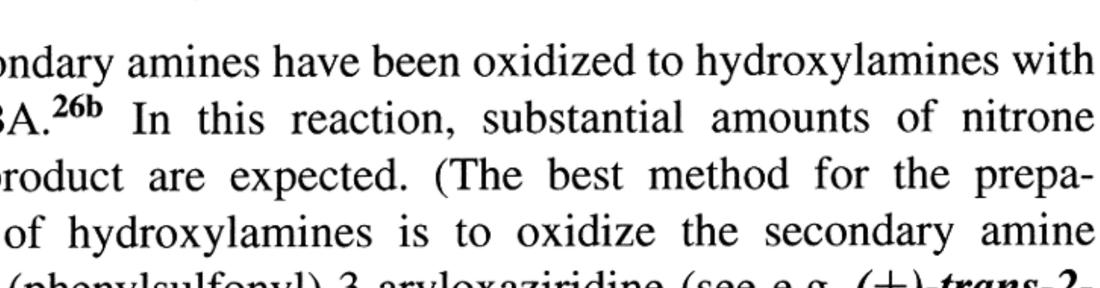
m-CPBA oxidation of the sulfilimine (**42**) prepared from 2-aminopyridine, furnished 2-nitrosopyridine (**43**) (eq 13).[50]



(42) (43) (13)

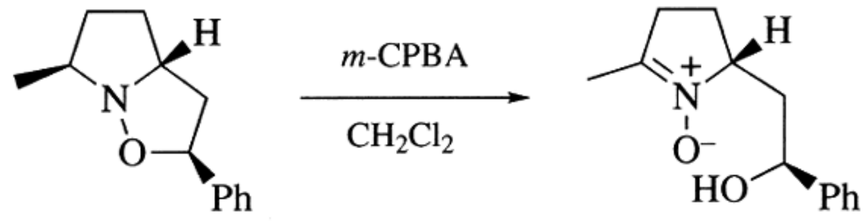
Secondary amines have been oxidized to hydroxylamines with *m*-CPBA.[26b] In this reaction, substantial amounts of nitrone as byproduct are expected. (The best method for the preparation of hydroxylamines is to oxidize the secondary amine with 2-(phenylsulfonyl)-3-aryloxaziridine (see e.g. ***(±)-trans-2-(Phenylsulfonyl)-3-phenyloxaziridine***) to the nitrone, and then to reduce the nitrone with ***Sodium Cyanoborohydride***).[51]

m-CPBA oxidation of N-heterocycles furnishes in high yields the corresponding *N*-oxides.[52] Several tertiary *N*-oxides have been prepared by the reaction of tertiary amines with *m*-CPBA in $CHCl_3$ at 0–25 °C and employing chromatography on alkaline alumina; for example, trimethylamine *N*-oxide was obtained in 96% yield.[53] When the optically pure tertiary amine (**44**) is oxidized with *m*-CPBA, the initially formed amine oxide rearranges to the hydroxylamine (**45**) with complete 1,3-transfer of chirality (eq 14).[54]

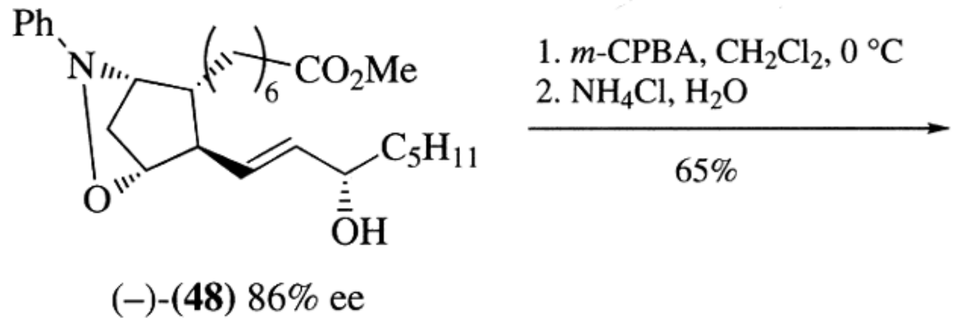


(44) (45) (14)

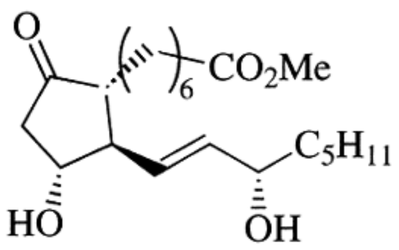
Reaction of *m*-CPBA with the isoxazole (**46**) furnishes the nitrone (**47**) (eq 15).[55] *m*-CPBA oxidation of (−)-isoxazole (**48**) and subsequent workup results in the formation of the (−)-cyclopentanone (**49**) (eq 16);[56] the initially formed nitrone is hydrolyzed during workup. The oxaziridine (**51**) has been prepared by epoxidizing the sulfonimine (**50**) (eq 17).[57]



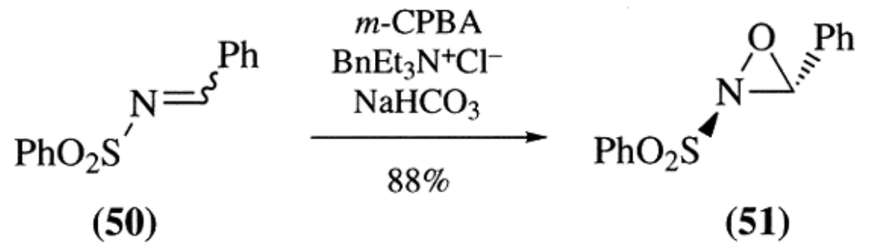
(46) (47) (15)



(–)-(**48**) 86% ee

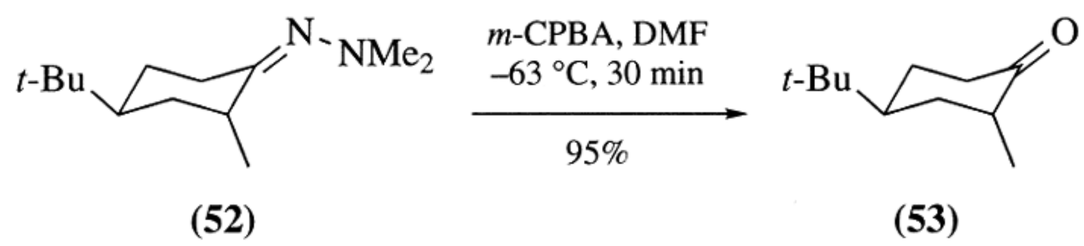


(–)-(**49**) 86% ee (16)



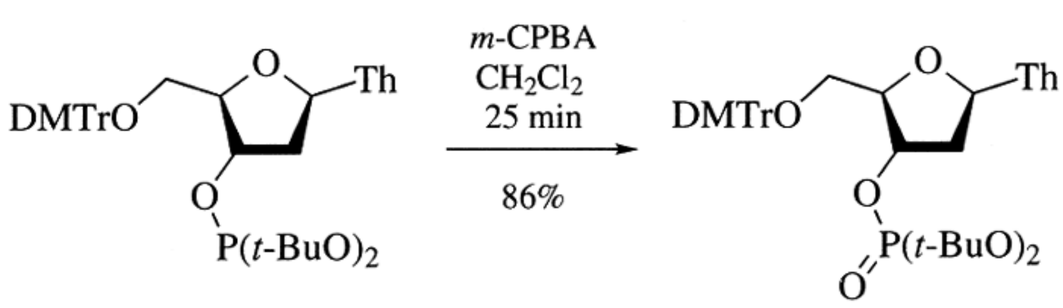
(50) (51) (17)

The cleavage of the *N,N*-dimethylhydrazone (**52**) proceeds rapidly in the presence of *m*-CPBA, even at low temperatures, to furnish the ketone (**53**), without isomerization to the more stable *cis* isomer (eq 18).[58]



(52) (53) (18)

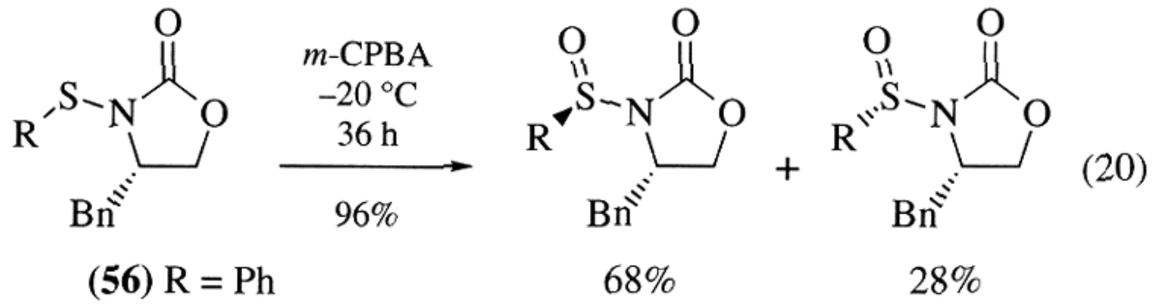
Oxidation of Phosphorus-Containing Compounds. *m*-CPBA oxidation of the phosphite (**54**) is stereospecific; it furnishes the phosphate (**55**) (eq 19).[59a] However, aqueous ***Iodine*** is the reagent of choice for the oxidation of nucleotidic phosphite triesters.[59b] *m*-CPBA oxidation of thiophosphate triesters furnishes the corresponding phosphate esters with retention of configuration.[60]



(54) (55) (19)

Oxidation of Sulfur-Containing Compounds. *n*-Butanethiol is oxidized by *m*-CPBA in CH_2Cl_2 at −30 °C to furnish in

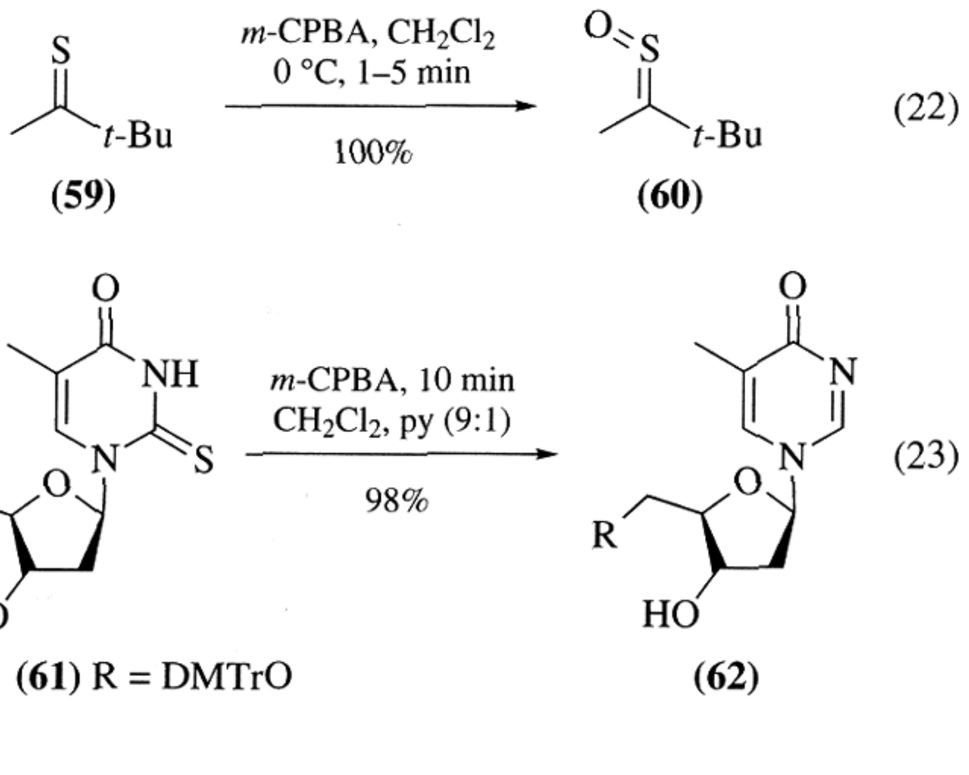
82% yield *n*-butanesulfinic acid (*n*-$BuSO_2H$); other thiols react similarly.[61] Sulfides are oxidized chemoselectively to sulfoxides by *m*-CPBA; the reaction is fast even at −70 °C, and the product is free from sulfone.[62] Three reagents (*m*-CPBA, ***Sodium Periodate***, and ***Iodosylbenzene***) are regarded as ideal for the oxidation of sulfides to sulfoxides.[63] Good diastereoselectivity has been observed in the oxidation of the sulfide (**56**) (eq 20).[64] Sulfides carrying suitably located hydroxyl groups are oxidized diastereoselectively, due to the directing influence of the hydroxyl group.[65] A phenyl sulfide carrying a variety of functional groups (epoxide, hydroxyl, ether, carbamate, and enediyne) has been chemoselectively oxidized in 99% yield to the corresponding sulfone.[52]



(**56**) R = Ph (20)

Allenyl chloromethyl sulfoxide (**57**) reacts with *m*-CPBA to furnish allenyl chloromethyl sulfone (**58**) (eq 21).[66] The enethiolizable thioketone (**59**) has been oxidized to the (*E*)-sulfine (**60**) (eq 22).[67] The 2′-deoxy-4-pyrimidinone (**62**) has been prepared by reacting the 2-thiopyrimidine nucleoside (**61**) with *m*-CPBA (eq 23).[68] Thioamides have been transformed to the amides in high yields.[69]

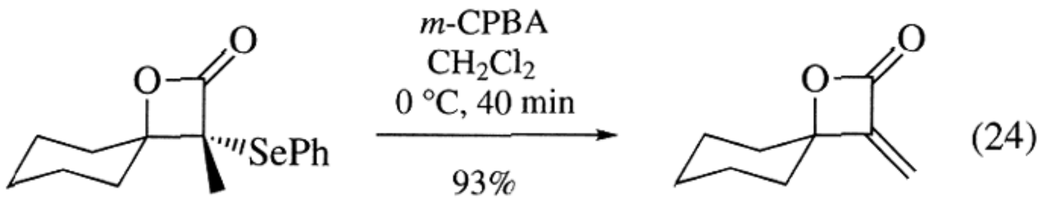
(**57**) (**58**) (21)



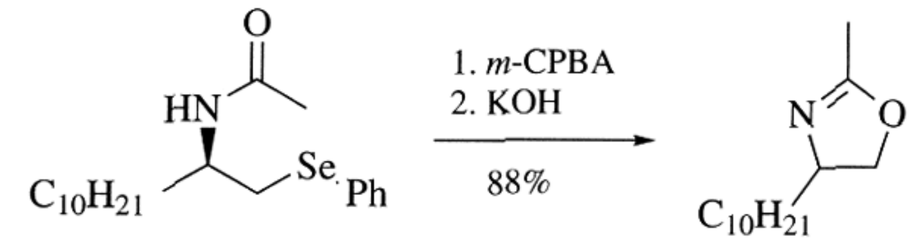
(**59**) (**60**) (22)

(**61**) R = DMTrO (**62**) (23)

Oxidation of Selenides. Phenyl selenides react rapidly with *m*-CPBA at −10 °C to form phenyl selenoxides,[70a] which on warming to 0 °C or at rt undergo facile *cis* elimination. This procedure for introducing unsaturation under mild conditions has been used in the synthesis of thermally sensitive compounds; for an example see eq 24.[70b] The selenonyl moiety is a good leaving group, and its generation in the substrate can lead to the formation of cyclic compounds. The oxazoline (**64**) has been synthesized through oxidation of the selenide (**63**) and treatment of the oxidized material with base (eq 25).[71]

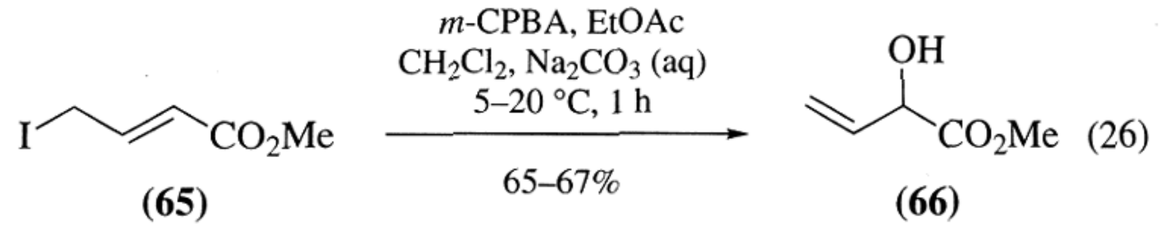


(24)



(**63**) (**64**) (25)

Oxidation of Allylic Iodides. *m*-CPBA oxidation of the primary allylic iodide (**65**) furnishes the secondary allylic alcohol (**66**) (eq 26);[72] this involves rearrangement of the iodoxy compound formed initially.



(**65**) (**66**) (26)

Comparison with Other Reagents. To effect epoxidation, the most commonly used reagents are *m*-CPBA, ***Peracetic Acid*** (PAA), and ***Trifluoroperacetic Acid*** (TFPAA). TFPAA is not commercially available. *m*-CPBA is more reactive than PAA and is the reagent of choice for laboratory-scale reactions. For large-scale epoxidations the cheaper PAA is preferred. The highly reactive TFPAA is used for unreactive and heat-sensitive substrates; its reactivity permits the use of low reaction temperatures. The recently introduced reagent magnesium monoperphthalate (MMPP) (see ***Monoperoxyphthalic Acid***) is more stable than *m*-CPBA and has many applications.[4]

Epoxidations of hydroxyalkenes have been carried out with ***t-Butyl Hydroperoxide***/vanadium (TBHP/V). *m*-CPBA epoxidation of (*Z*)-cyclooct-2-en-1-ol is *anti* selective; with TBHP/V it is *cis* selective.[24b] Similar differences have been noticed in some acyclic systems.[27c] Since the directing effect of the hydroxyl group is larger in the TBHP/V system it is a better reagent for hydroxyl-directed regioselective epoxidations of polyunsaturated alcohols;[73] the TBHP/V system also exhibits higher hydroxyl-directed selectivity in highly hindered allylic alcohols.[74]

m-CPBA epoxidation of hindered alkenes takes place selectively from the less hindered side; the epoxide of opposite stereochemistry can be prepared by a two-step procedure involving initial preparation of bromohydrin, followed by base treatment.[28]

For the epoxidation of extremely unreactive alkenes[38b] and for the preparation of epoxides which are highly susceptible to nucleophilic attack, ***Dimethyldioxirane*** is the reagent of choice.[75] Electron-deficient alkenes such as α,β-unsaturated ketones are usually oxidized with ***Hydrogen Peroxide***/base.

Related Reagents. See Classes O-8, O-11, O-14, O-15 and O-20, pages 1–10. *m*-Chloroperbenzoic Acid–2,2,6,6-Tetramethylpiperidine Hydrochloride.

1. (a) Swern, D. *Organic Peroxides*; Wiley: New York, 1971; Vol 2, pp 355–533. (b) Plesnicar, B. *Organic Chemistry*; Academic: New York, 1978; Vol. 5 C, pp 211–294. (c) Rao, A. S. *COS* **1991**, *7*, Chapter 3.1.
2. McDonald, R. N.; Steppel, R. N.; Dorsey, J. E. *OS* **1970**, *50*, 15.
3. (a) Schwartz, N. N.; Blumbergs, J. H. *JOC* **1964**, *29*, 1976. (b) Nakayama, J.; Kamiyama, H. *TL* **1992**, *33*, 7539.

4. Brougham, P.; Cooper, M. S.; Cummerson, D. A.; Heany, H.; Thompson, N. *S* **1987**, 1015.
5. *Hazards in the Chemical Laboratory*; Luxon, S. G., Ed.; Royal Society of Chemistry: Cambridge, 1992.
6. (a) Ishikawa, K.; Charles, H. C.; Griffin, G. W. *TL* **1977**, 427. (b) Srebnik, M.; Mechoulam, R.; *S* **1983**, 1046.
7. Berti, G. *Top. Stereochem.*, **1973**, *7*, 93.
8. (a) Woods, K. W.; Beak, P. *JACS* **1991**, *113*, 6281. (b) Bartlett, P. D. *Rec. Chem. Prog.* **1950**, *11*, 47 (cited in Ref. 1a).
9. (a) Camps, F.; Coll, J.; Messeguer, A.; Pujol, F. *JOC* **1982**, *47*, 5402. (b) Chai, K.-B.; Sampson, P. *TL* **1992**, *33*, 585.
10. Paquette, L. A.; Barrett, J. H. *OS* **1969**, *49*, 62.
11. (a) Wender, P. A.; Zercher, C. K. *JACS* **1991**, *113*, 2311. (b) Philippo, C. M. G.; Vo, N. H.; Paquette, L. A. *JACS* **1991**, *113*, 2762.
12. Bach, R. D.; Knight, J. W. *OS* **1981**, *60*, 63.
13. (a) Kishi, Y.; Aratani, M.; Tanino, H.; Fukuyama, T.; Goto, T. *CC* **1972**, 64. (b) Valente, V. R.; Wolfhagen, J. L. *JOC* **1966**, *31*, 2509.
14. Anderson, W. K.; Veysoglu, T. *JOC* **1973**, *38*, 2267. (b) Imuta, M.; Ziffer, H. *JOC* **1979**, *44*, 1351.
15. Urones, J. G.; Marcos, I. S.; Basabe, P.; Alonso, C.; Oliva, I. M.; Garrido, N. M.; Martin, D. D.; Lithgow, A. M. *T* **1993**, *49*, 4051.
16. Bäckvall, J.-E.; Juntunen, S. K. *JOC* **1988**, *53*, 2398.
17. Hudlicky, T.; Price, J. D.; Rulin, F.; Tsunoda, T. *JACS* **1990**, *112*, 9439.
18. Marsh, E. A. *SL* **1991**, 529.
19. Brown, H. C.; Kawakami, J. H.; Ikegami, S. *JACS* **1970**, *92*, 6914.
20. Devreese, A. A.; Demuynck, M.; De Clercq, P. J.; Vandewalle, M. *T* **1983**, *39*, 3049.
21. Still, W. C.; Romero, A. G. *JACS* **1986**, *108*, 2105.
22. Schneider, A.; Séquin, U. *T* **1985**, *41*, 949.
23. Johnson, C. R.; Tait, B. D.; Cieplak, A. S. *JACS* **1987**, *109*, 5875.
24. (a) Henbest, H. B.; Wilson, R. A. L. *JCS* **1957**, 1958. (b) Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S. *JACS* **1979**, *101*, 159.
25. Wipf, P.; Kim, Y. *JOC* **1993**, *58*, 1649.
26. (a) Kim, G.; Chu-Moyer, M. Y.; Danishefsky, S. J.; Schulte, G. K. *JACS* **1993**, *115*, 30. (b) Fukuyama, T.; Xu, L.; Goto, S. *JACS* **1992**, *114*, 383.
27. (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (b) Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *TL* **1979**, 4733. (c) Adam, W.; Nestler, B. *JACS* **1993**, *115*, 5041.
28. Kočovský, P.; Starý, I. *JOC* **1990**, *55*, 3236.
29. Murphy, P. J.; Russel, A. T.; Procter, G. *TL* **1990**, *31*, 1055.
30. Fleming, I.; Sarkar, A. K.; Thomas, A. P. *CC* **1987**, 157.
31. Johnson, M. R.; Kishi, Y. *TL* **1979**, 4347.
32. Roush, W. R.; Straub, J. A.; Brown, R. J. *JOC* **1987**, *52*, 5127.
33. Sakai, N.; Ohfune, Y. *JACS* **1992**, *114*, 998.
34. Lewis, M. D.; Menes, R. *TL* **1987**, *28*, 5129.
35. Fukuyama, T.; Wang, C.-L. J.; Kishi, Y. *JACS* **1979**, *101*, 260.
36. Paquette, L. A.; Lin, H.-S.; Gallucci, J. C. *TL* **1987**, *28*, 1363.
37. (a) Rubottom, G. M.; Gruber, J. M. *JOC* **1978**, *43*, 1599. (b) Rubottom, G. M.; Gruber, J. M.; Juve, H. D.; Charleson, D. A. *OS* **1986**, *64*, 118.
38. (a) Herlem, D.; Kervagoret, J.; Yu, D.; Khuong-Huu, F.; Kende, A. S. *T* **1993**, *49*, 607. (b) Crimmins, M. T.; Jung, D. K.; Gray, J. L. *JACS* **1993**, *115*, 3146.
39. Rubottom, G. M.; Marrero, R. *JOC* **1975**, *40*, 3783.
40. Hassner, A.; Reuss, R. H.; Pinnick, H. W. *JOC* **1975**, *40*, 3427.
41. Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *TL* **1989**, *30*, 3323.
42. Shimshock, S. J.; Waltermire, R. E.; DeShong, P. *JACS* **1991**, *113*, 8791.
43. Honda, T.; Kobayashi, Y.; Tsubuki, M. *T* **1993**, *49*, 1211.
44. Zhou, W.-S.; Lu, Z.-H.; Wang, Z.-M. *T* **1993**, *49*, 2641.
45. Krow, G. R. *COS* **1991**, *7*, Chapter 5, 1.
46. Feldman, K. S.; Wu, M.-J.; Rotella, D. P. *JACS* **1990**, *112*, 8490.
47. Bakale, R. P.; Scialdone, M. A.; Johnson, C. R. *JACS* **1990**, *112*, 6729.
48. Gilbert, K. E.; Borden, W. T. *JOC* **1979**, *44*, 659.
49. Robinson, C. H.; Milewich, L.; Hofer, P. *JOC* **1966**, *31*, 524.
50. Taylor, E. C.; Tseng, C.-P.; Rampal, J. B. *JOC* **1982**, *47*, 552.
51. Jasys, V. J.; Kelbaugh, P. R.; Nason, D. M.; Phillips, D.; Rosnack, K. J.; Saccomano, N. A.; Stroh, J. G.; Volkmann, R. A. *JACS* **1990**, *112*, 6696.
52. Nicolaou, K. C.; Maligres, P.; Suzuki, T.; Wendeborn, S. V.; Dai, W.-M.; Chadha, R. K. *JACS* **1992**, *114*, 8890.
53. Craig, J. C.; Purushothaman, K. K. *JOC* **1970**, *35*, 1721.
54. Reetz, M. T.; Lauterbach, E. H. *TL* **1991**, *32*, 4481.
55. Ali, Sk. A.; Wazeer, M. I. M. *T* **1993**, *49*, 4339.
56. Hwu, J. R.; Robl, J. A.; Gilbert, B. A. *JACS* **1992**, *114*, 3125.
57. Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *OS* **1988**, *66*, 203.
58. Duraisamy, M.; Walborsky, H. M. *JOC* **1984**, *49*, 3410.
59. (a) Sekine, M.; Iimura, S.; Nakanishi, T. *TL* **1991**, *32*, 395. (b) Beaucage, S. L.; Iyer, R. P. *T* **1992**, *48*, 2223.
60. Cullis, P. M. *CC* **1984**, 1510.
61. Filby, W. G.; Günther, K.; Penzhorn, R. D. *JOC* **1973**, *38*, 4070.
62. Trost, B. M.; Salzmann, T. N.; Hiroi, K.; *JACS* **1976**, *98*, 4887.
63. Madesclaire, M. *T* **1986**, *42*, 5459.
64. Evans, D. A.; Faul, M. M.; Colombo, L.; Bisaha, J. J.; Clardy, J.; Cherry, D. *JACS* **1992**, *114*, 5977.
65. (a) Wang, X.; Ni, Z.; Lu, X.; Smith, T. Y.; Rodriguez, A.; Padwa, A. *TL* **1992**, *33*, 5917. (b) DeLucchi, O.; Fabri, D. *SL* **1990**, 287.
66. Block, E.; Putman, D. *JACS* **1990**, *112*, 4072.
67. Le Nocher, A. M.; Metzner, P. *TL* **1991**, *32*, 747.
68. Kuimelis, R. G.; Nambiar, K. P. *TL* **1993**, *34*, 3813.
69. Kochhar, K. S.; Cottrell, D. A.; Pinnick, H. W. *TL* **1983**, *24*, 1323.
70. (a) Reich, H. J.; Shah, S. K. *JACS* **1975**, *97*, 3250. (b) Danheiser, R. L.; Choi, Y. M.; Menichincheri, M.; Stoner, E. J. *JOC* **1993**, *58*, 322.
71. Toshimitsu, A.; Hirosawa, C.; Tanimoto, S.; Uemura, S. *TL* **1992**, *33*, 4017.
72. Yamamoto, S.; Itani, H.; Tsuji, T.; Nagata, W. *JACS* **1983**, *105*, 2908.
73. Boeckman, Jr. R. K.; Thomas, E. W. *JACS* **1979**, *101*, 987.
74. Sanghvi, Y. S.; Rao, A. S. *JHC* **1984**, *21*, 317.
75. (a) Murray, R. W. *CR* **1989**, *89*, 1187. (b) Halcomb, R. L.; Danishefsky, S. J. *JACS* **1989**, *111*, 6661. (c) Adam, W.; Hadjiarapoglou, L.; Wang, X. *TL* **1989**, *30*, 6497. (d) Adam, W.; Curci, R.; Edwards, J. O. *ACR* **1989**, *22*, 205.

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