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Epoxidation of substituted norbornenes. Stereochemical aspects and accompanying intramolecular transformations

L I Kasyan

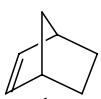
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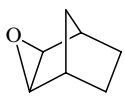
Abstract. Traditional and new procedures for epoxidation of substituted norbornenes are described. The stereochemistry of this reaction and the influence of substituents on the reactivity of the substrate are analysed. The molecular rearrangements and heterocyclisation reactions that can accompany epoxidation are considered; examples of selective attack of oxidants at one of the double bonds in norbornenes containing an unsaturated substituent and also at a multiple bond in some polycyclic di- and triene systems are given. The bibliography includes 252 references.

I. Introduction

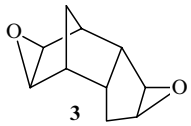
A great number of studies have been devoted to norbornene **1**, epoxynorbornane **2**, and their derivatives. This is mostly due to the fact that processing of norbornene-based epoxides gives practically valuable products and also to the fact that these compounds are readily produced from cyclopentadiene, which is a large-scale side product of the coke and petroleum processing industries. Thus dicyclopentadiene diepoxide **3** found application for the industrial manufacture of various polymeric compositions as early as the 1970s.



1



exo-**2**



3

The special position occupied by norbornene and its derivatives in the synthesis of epoxides is due to the high reactivity of the strained double bond, stereoselectivity of the attack by oxidants, high stability of the resulting epoxides in neutral and alkaline media, and their clear-cut susceptibility to skeletal rearrangements in the presence of acids. No reviews specially devoted to epoxidation of substituted norbornenes have been published; some information on this point can be found in reviews dealing with more general topics.[1–10] The interest in the use of various epoxidising agents for preparing compounds of this type becomes even greater because the known attempts to use the halohydrin method in the synthesis of some epoxynorbornanes have failed. In the case of stereoisomeric *exo*- and *endo*-bicyclo[2.2.1]hept-2-ene-5-carbonitriles, bromohydration is accompanied by Wagner–Meerwein rearrangement and yields adducts with a non-vicinal arrangement of the bromine and the hydroxyl precluding their transformation into epoxides in the presence of bases.[11]

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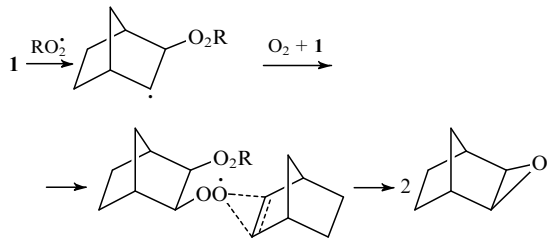
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II. Methods for synthesis of epoxynorbornanes

Epoxynorbornane (2,3-epoxybicyclo[2.1.1]heptane or 3-oxatricyclo[3.2.1.0^{2,4}]octane) was first synthesised in 1954 by two research groups working independently by treatment of norbornene with peroxy acids.[12,13] Later, norbornene has become a convenient model for the investigation of the mechanism of epoxidation of alkenes.[1,4,5,14–17] This is due to the fact that among cycloalkenes, norbornene is the most reactive towards oxidation, irrespective of the particular oxidant used. This high reactivity of norbornene is explained by its strained character, caused by the fact that, according to a number of theoretical and experimental studies,[18] the double bond in this molecule is non-planar (the strained state of the norbornene molecule is also manifested in spectroscopic and chemical characteristics[18–22]). Norbornene has been epoxidised by, for example, organic peroxy acids[23–29] (including those supported on polymeric substrates[30]), alkyl hydroperoxides,[2,6,31–33] peroxyimidic acids in two-phase systems,[34] α-hydroperoxydiazenes,[35] and α-azo-hydroperoxides.[36] Quite promising for this purpose are Caro's acid,[37] peroxysulfur intermediates based on the superoxide anion (O_2^-),[38] as well as the new large class of dioxiranes generated from salts of Caro's acid and acetone.[39] Murray and coworkers[39] demonstrated the possibility of obtaining the labile monoepoxide and (previously unknown) diepoxide of norbornadiene using dimethyldioxirane. This permits the above experimental procedure to be highly appreciated (some modifications of this method have been reported, in particular, epoxidation of norbornene and other alkenes *via* oxaziridinium salts[40]). The use of sodium perborate as the oxidant also seems quite promising.[41]

Molecular oxygen is used both for spontaneous oxygenation of norbornene (which is due to the highly strained character of

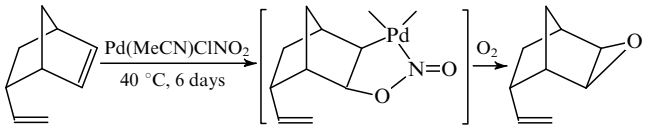
alkenes of this series)[42] and for sensitised oxidation.[43–45] Study of the latter reaction demonstrated that it occurs as stereospecific *exo*-addition of the peroxyl radical to the strained π-bond of the substrate:



The oxidation of norbornene by oxygen has been carried out in the presence of silver catalysts[46,47] and also specially prepared titanium silicate.[48] Photooxidation of norbornene catalysed by various compounds,[49] in particular, sulfur dioxide[50] has also been studied. Epoxidation of norbornene and other cycloalkenes using the oxygen of water as the oxidant in the presence of platinum complexes has been reported.[51]

In a number of studies, oxidation of norbornene derivatives by singlet oxygen has been described.[52,53] The reaction with singlet oxygen in the presence of phosphites was assumed to involve the *in situ* formation of phosphadioxirane intermediates.[54]

A convenient method for epoxidation of norbornene and its derivatives by oxygen in the presence of nitropalladium complexes has been proposed.[55–58] The strained double bond in norbornene, vinylnorbornene, and methylnorbornene ensures the formation of a stable five-membered transition state, the yield of epoxide reaching 50%.

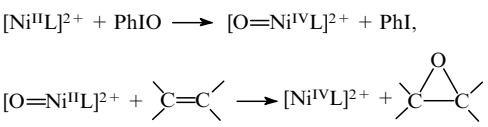


This method has also been used to oxidise a number of terminal alkenes and substituted cyclohexenes: the former are converted into ketones, while the latter form mixtures of epoxides, ketones, enols, and other products or do not react at all.[55]

The reactivity of the intermediate complex can be changed by adding copper(II) chloride; in the presence of this salt, the thermal destruction leading to the epoxide is completely suppressed, and rearrangement of the substrate occurs instead.[56]

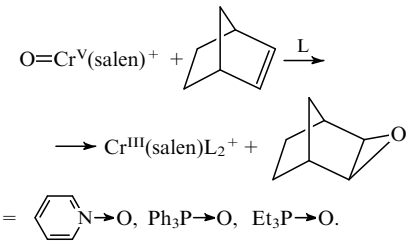
Takai *et al.*[59,60] found that norbornene and its derivatives are easily transformed into epoxides upon treatment with oxygen (as oxidant) and secondary or primary alcohols (as reducing agents) in the presence of catalytic amounts of 1,3-diketonatooxovanadium(IV) complexes. Later, a similar transformation was accomplished using nickel[61] or iron[62] complexes as catalysts in the presence of aldehydes. The reactions were carried out under atmospheric pressure at a moderate temperature, and the epoxides were obtained in high (up to quantitative) yields.[63] Heteropoly compounds of the type $(NH_4)_5H_4PV_6W_6O_{40}$ were also proposed as catalysts for this process.[64]

An important aspect of the chemistry of norbornene derivatives is investigation of the regularities of liquid-phase catalytic oxidation reactions in which peroxides of transition metals (copper, nickel, cobalt, chromium, molybdenum, vanadium, rhenium, and manganese) are formed as active intermediates.[31,65–77] Nickel(II) complexes with tetraaza-macrocycles, Schiff bases, and bidentate phosphines have also been studied.[31,68] Thus in the oxidation of norbornene with iodosylbenzene in the presence of a nickel complex, the complex is activated by reducing iodosylbenzene to iodobenzene. During the transfer of oxygen, the resulting oxo-nickel(IV) intermediate experiences the influence of various factors: the nature of the solvent, concentrations of the reactants, and the temperature. In particular, when H_2O[18] is used, the labelled oxygen atom proves to be incorporated in the epoxide (80%).



This method cannot be used to epoxidise cycloalkenes. For example, cyclohexene is converted under these conditions into a mixture of the epoxide, cyclohex-2-enol, and the corresponding ketone (the yields are 36%, 49%, and 15%, respectively).[68]

The use of chromium(III) salicylaldimine complexes (salen)Cr^{III} has several advantages over the method described above (the yield of epoxynorbornane increases to 85%, and the method becomes applicable to some cycloalkenes). The catalytically active species in this reaction are chromium(V) oxo complexes resulting from interaction of the initial complexes (salen)Cr^{III} with iodosylbenzene. When pyridine, triphenylphosphine, or trimethylphosphine oxides are used as the ligands L, the activity of the complex increases by several orders of magnitude.[71]

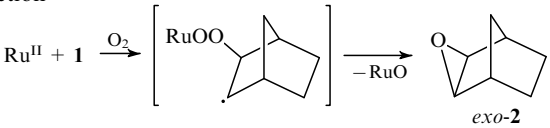


The use of cyanopyridinium chlorochromate as the oxidant for norbornene and other cycloalkenes leads to products of another type, namely, chloro ketones.[78]

Agarval *et al.* have studied oxidation of cycloalkanes catalysed by Fe(III),[79] Cr(III),[80] Mn(III),[81,82] and Ru(III)[83] complexes with Schiff bases. Later, manganese complexes with Mannich bases have also been tested as catalysts for this reaction.[84] Among the cycloalkenes studied, norbornene was found to be the most reactive, and, what is especially important, to undergo the most selective epoxidation.[79]

The epoxidation of alkenes with aqueous solutions of hydrogen peroxide, is accomplished using heteropolytungsten complexes of transition metals (chromium, iron), because they are stable with respect to solvolysis,[85,86] and also complexes based on Ru(III) and Ru(II).[87–90]

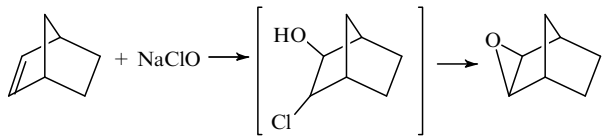
Drago *et al.*[90] successfully epoxidised norbornene using oxygen and sterically hindered ruthenium complexes (the selectivity of epoxide formation was 94%). The homolytic mechanism of this reaction



exo-**2**

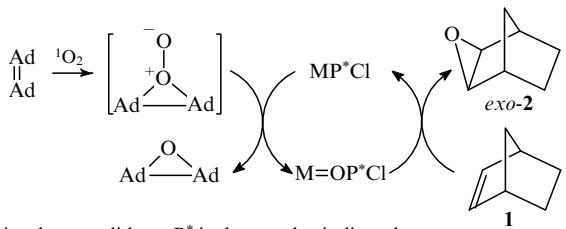
was confirmed experimentally.

At present, considerable attention is paid to the use of metal porphyrins as catalysts for this reaction, because oxidation involving these compounds is quite similar to the enzymic epoxidation and hydroxylation catalysed by cytochrome P-450[91] or P-420.[92] Considerable progress has already been achieved along this line: methods for asymmetric epoxidation have been developed;[91] biomimetic electrochemical systems for the oxidation of hydrocarbons, in particular norbornene, by molecular oxygen have been constructed;[93] (usually, iodosylbenzene, peroxy acids, or alkyl hydroperoxides are used for oxidation).[94] The hypothesis of formation of the chlorohydrin intermediate during the oxidation of norbornene by sodium hypochlorite have been rejected based on stereochemical considerations.[95]



Photocatalytic oxygenation of norbornene by molecular oxygen in the presence of iron tetraarylporphyrinates has been studied.[92] Whereas cyclohexene and cycloheptene are oxidised to give mixtures of products containing only 20%–35% of the epoxide, norbornene **1** is entirely converted into epoxynorbornane **2** under the same conditions.

Ando *et al.*[96] proposed a peculiar scheme for the preparation of the compound **2** by joint oxidation of norbornene **1** and adamantylideneadamantane in the presence of iron(III) porphyrins. The results of kinetic studies suggest that the first stage consists in oxidation of adamantylideneadamantane; after that, the oxygen atom from the perepoxy intermediate thus formed is transferred to the metal porphyrin, and then norbornene is oxidised:

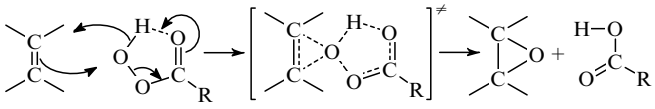


Ad is adamantylidene, P^* is the porphyrin ligand.

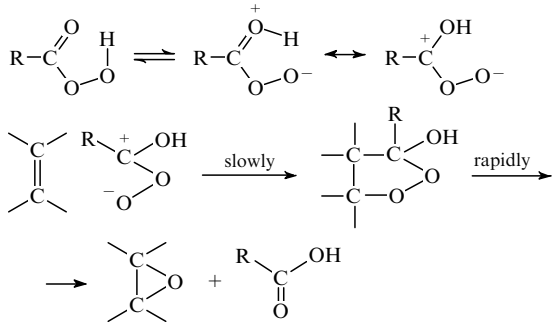
Interesting results have been obtained with ruthenium porphyrin complexes as the catalysts.[97,98] Oxidation of ruthenium tetramesitylporphyrinate by *m*-chloroperbenzoic acid (MCPBA) yielded stable crystalline dihydroxoruthenium(IV) tetramesitylporphyrinate, which was used to carry out aerobic oxidation of norbornene.[98]

III. Reaction mechanism

Norbornene is a convenient model to study the mechanism of epoxidation. This process is described most often in terms of the scheme proposed by Lynch and Pausacker,[17] who rationalised epoxidation of alkenes with peroxy acids as a synchronous process including formation of a three-membered cyclic transition state.

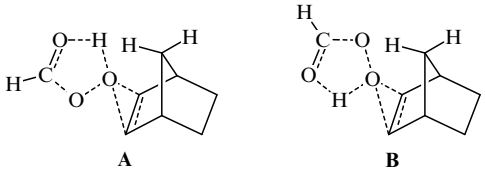


Since the above simple scheme is suitable only for describing processes carried out in weakly polar solvents, Kwart *et al.*[99,100] proposed a different mechanism according to which this reaction is rationalised as dipolar 1,3-cycloaddition; this was confirmed by calculations.[17]



The structure of the cyclic transition state (three- or five-membered) has been discussed on the basis of a study of epoxidation kinetics, norbornene being used as the model compound. It was found that the ratio of the rate constants for epoxidation of norbornene and cyclohexene by peroxylaurinic acid, equal to 1.2, differs sharply from the corresponding ratios found for the reactions of the same substrates with phenyl azide (6.5×10^3) or picryl azide (8.0×10^3).[101] This is evidence against the 5-membered transition state in epoxidation. In fact, the strain in the three-membered transition state should smooth out the differences between the epoxidation patterns observed for various types of alkenes. Later, similar kinetic calculations served as the key for elucidation of the mechanism of oxidation of alkenes with ozone,[102] xenon trioxide,[103] osmium tetroxide,[102] and chromic acid.[104]

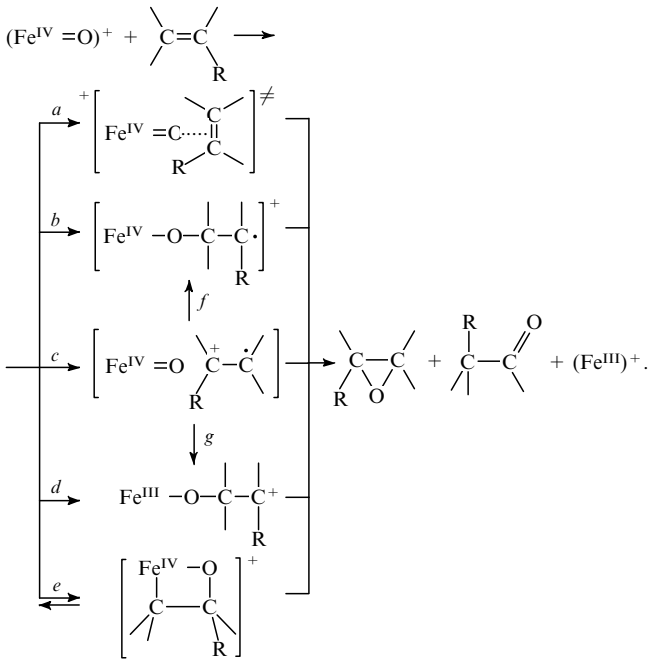
Epoxidation of norbornene and its derivatives by performic acid has been studied.[105] Two variants (**A** and **B**) for the primary orientation of norbornene in relation to the plane of the peroxycarbonyl group atoms are possible.



According to calculations, both transition states are first-order saddle points; however, in the former case the activation enthalpy ($\Delta H^{\neq}$) is lower by 4.7 kJ mol^{-1}.

In the case of iron porphyrinates,[106] the mechanism of epoxidation includes the formation of a high-valence metal porphyrin radical cation, for example, $(Fe^{IV}=O)^+$, which acts as the direct oxidising agent, different key steps of the reaction being possible.

This might be the direct transfer of the oxygen atom [path (*a*)], homolytic addition followed by fast closure of the epoxide ring [path (*b*)], electrophilic addition and subsequent cyclisation [path (*d*)], reversible formation of metal oxetane followed by recyclisation and epoxide formation [path (*e*)] and electron transfer [path (*c*)] followed by transformation into a radical cation [path (*f*)] or a carbocation [path (*g*)].[104]

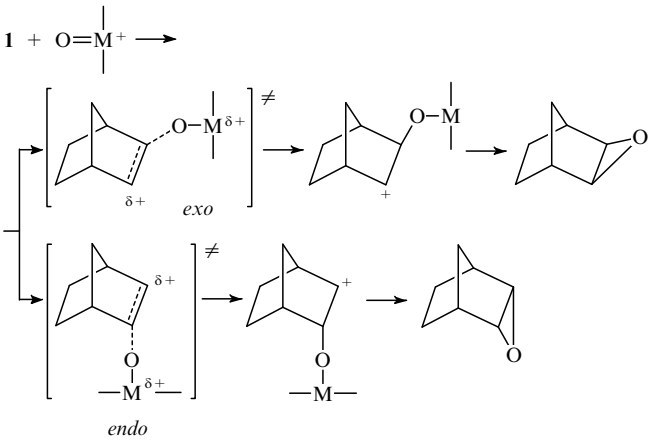


In this case, unlike the traditional scheme for epoxidation by peroxy acids, a mechanism involving the intermediate formation of a radical cation [path (*f*)] has also been proposed.[107] This is confirmed by the composition of the reaction products and by kinetic data obtained for epoxidation of various alkenes. The logarithms of the rate constants for the epoxidation were found to

obey a linear correlation with the ionisation potentials of the alkenes.

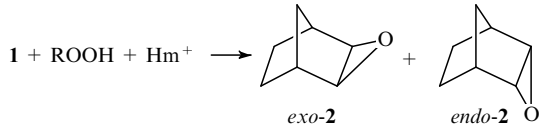
The reaction mechanism was developed with allowance for the stereochemical data obtained for epoxidation of norbornene.[107, 108] Traylor *et al.*[109] showed that the *exo*-stereoselectivity of epoxidation, typical of norbornene, does not hold in the presence of metal porphyrins, and the ratio of the yields of *exo*- and *endo*-epoxynorbornanes depends appreciably on the type of metal incorporated in the porphyrin nucleus and the type of substituents in the benzene rings of a substituted tetraphenylporphyrin.[109] Thus the ratio of *exo*- to *endo*-epoxynorbornanes amounts to ~1000 for electropositive Cr complexes and ~6 for electronegative Fe(III) complexes, the amount of the rearranged products decreasing in parallel. When norbornene is oxidised by pentafluoroiodobenzene in the presence of iron tetra(4-methylphenyl)- or tetra(2,6-dichlorophenyl)porphyrinates, the yield of the epoxide is 45% or 82%, and the ratio of *exo*- to *endo*-stereoisomers is 71 or 9, respectively (in the case of oxidation by peroxy acids, this ratio is 600–700). Moreover, it was found that the logarithm of the (*exo*/*endo*) ratio correlates with the σ-Hammett constants of the substituents in the porphyrin benzene rings.[109]

This finding can be explained by assuming a change of the reaction mechanism: in place of the electron transfer [path (*f*)], electrophilic attack [path (*d*)] occurs, resulting in the formation of a transition state consisting of the alkene weakly bound to the attacking reagent.



The electron density on the central metal atom in metal porphyrins increases in the following sequence of metals: iron(III) < manganese(III) < chromium(III). In the same series, the bond between the alkene and the attacking reagent in the transition state becomes stronger and the C···O distance decreases; simultaneously, steric hindrance becomes more significant, and the *exo*-stereoselectivity is enhanced.[109]

Traylor *et al.*,[109] who studied oxidation of norbornene with hydrogen peroxide and *tert*-butyl hydroperoxide catalysed by iron porphyrinate with fluorinated benzene rings, obtained the same *exo* : *endo* ratio (22 : 1) as was found using pentafluoroiodobenzene as the oxidant.[109] As has been shown previously, this oxidising agent reacts with the porphyrinates giving iron(IV) radical cation (oxene). Traylor *et al.*[110] were able to demonstrate that in the presence of iron porphyrinates, including hemin (Hm^+), as the catalysts, hydrogen peroxide and *tert*-butyl hydroperoxide undergo heterolytic cleavage to give oxene:

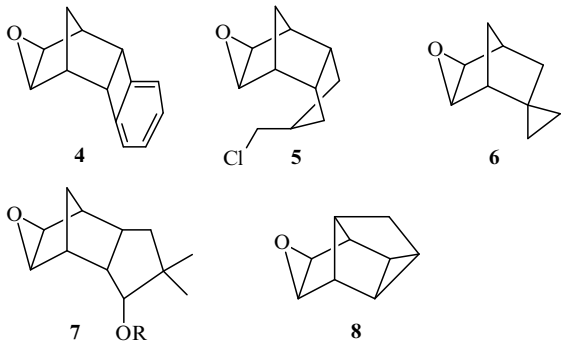


The approach to the mechanism of norbornene oxidation outlined above has been confirmed by investigating this reaction in the presence of new porphyrin catalysts [111] and new oxidants.[112]

In a study of joint oxidation of α-methylstyrene and norbornene with MCPBA or *o*-chloroperbenzoic acid in the presence of iron(III) porphyrinates, it was found that the selectivity of epoxidation changes crucially depending on the solvent.[113] It was found that the formation of oxoferryl porphyrin radical cation is not the preferential route.

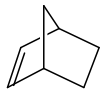
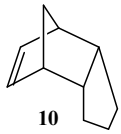
In some cases, fine structural features of the ligand have a substantial influence on the stereochemistry of epoxidation of norbornene.[114] In particular, the use of isomeric ligands incorporating 3- and 4-pyridyl fragments leads to different results: in the former case, a mixture of stereoisomeric epoxides is formed, while in the latter case, only the *exo*-isomer is produced. Agarwal *et al.*[114] explained these differences by specific features of coordination of the nitrogen atoms of the pyridine ligands to the manganese atom.

When MCPBA was used as the oxidant, the reaction gave various polycyclic structures (for example, **4**–**8**) incorporating epoxynorbornane or related fragments.[115–120]



IV. Stereochemistry of epoxidation of substituted norbornenes with peroxy acids

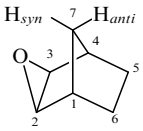
The stereochemical outcome of the epoxidation of substituted norbornenes with peroxy acids, namely, the formation of an *exo*-epoxide ring, is a particular case of the known Alder rule.[121] It has been discussed in detail in a number of studies.[122–125] Earlier, the configuration of the epoxides has been studied by converting them into known norbornanols; thus, it was found that the epoxynorbornane formed contains only a slight amount of the *endo*-epoxide (6%,[126] 0.5% [127]). Brown *et al.*[127] attributed the *exo*-attack to the predominant steric hindrance of the *endo*-area by the norbornene fragment. As model compounds, they chose norbornene (**1**), *cis*-bicyclo[3.3.0]octene, and *endo*-5,6-trimethylenonorbornene **10**. The increase in the steric hindrance of the *endo*-area of the ring was judged by the increase in the *exo*-stereoselectivity.[127]

Compound	 **9**	 **1**	 **10**
exo : *endo* ratio of epoxides	87 : 13	99.5 : 0.5	99.9 : 0.1

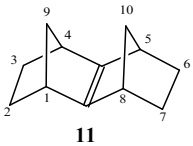
Later, the selectivity of the attack and the high reactivity of norbornene have been explained by the influence of hyperconjugation and out-of-plane deformation. Theoretical studies showed that the =C–H bonds in norbornene, unlike those in cyclohexene or bicyclo[2.2.2]octene, are bent by 2–5° to the *endo*-area. In the transition state, the *endo*-bending ensures both *exo*-stereoselectivity and a high rate of the attack by an electrophilic reagent. The presence of the *endo*-bending was attributed to the repulsion between the π-orbital and the occupied orbitals of the methylene bridge.

In fact, the vast majority of known epoxynorbornanes have *exo*-configuration in which the protons of the $C(7)H_2$ bridge are appreciably non-equivalent, one of them being arranged directly

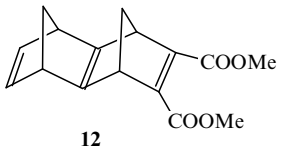
above the plane of the epoxide fragment and experiencing substantial paramagnetic shielding.



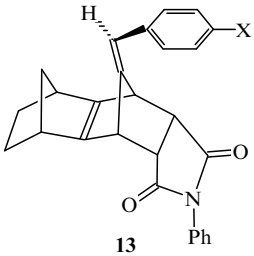
The non-equivalence of the bridging protons in the ^1H NMR spectrum as well as the unusual shielding of the C(7) atom in the ^{13}C NMR spectrum are the two criteria, which can be used to determine the stereochemistry of an epoxynorbornane fragment.[125, 128] The *exo*-configuration has been confirmed by X-ray diffraction analysis.[129, 130] *exo*-Stereoselective epoxidation has also been observed for the 7-oxa analogue of norbornene [131] and for polycyclic compounds, related to norbornene but much more complicated, such as *syn*-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanonaphthalene **11** and its derivatives **12** and **13**.



11

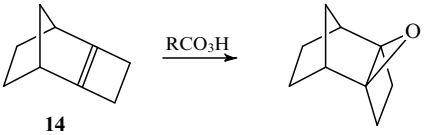


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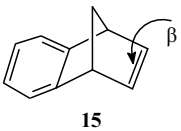
13

In this case, the *endo*-shielding is even more significant: the distances between the internal hydrogen atoms H(9), H(10) and H(3), H(6) are 3.416 and 2.728 Å,[132] respectively; since, the $sp^2 \rightarrow sp^3$ transition relieves strain, these alkenes and polyenes are readily epoxidised.[133, 134] The presence of a fulvene group in the compound **13** does not change the stereoselectivity of the attack by oxidants (peroxy acids, oxygen) directed at the strained double bond.[135] The *exo*-attack is also characteristic of the strained system **14** with a cyclobutene fragment.[136]

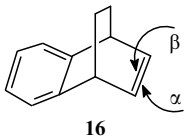


14

As the ring becomes less strained and/or shielding of the two directions of the attack becomes equal, this stereochemical course no longer predominates; thus bicyclo[2.2.2]octene **16**, unlike benzonorbornene **15**, undergoes non-stereospecific epoxidation giving rise to *exo*(β)- and *endo*(α)-epoxides.[13, 137]

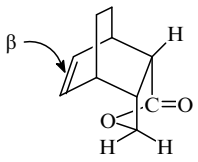


15



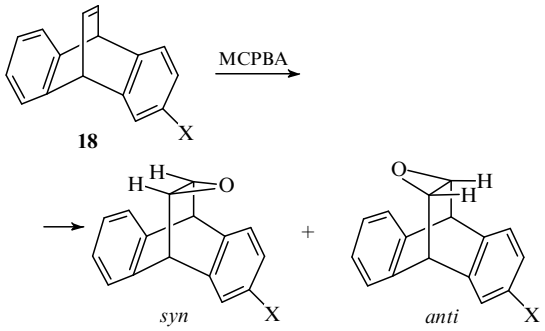
16

The stereochemistry of epoxidation of the anhydride or esters of *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic acid with trifluoroperoxyacetic acid is also non-stereospecific; the reaction mixture contains both epoxides together with products of lactonisation, whereas in the case of unsaturated lactone **17**, only the β-attack is observed, due to steric interactions involving the internal hydrogen atom of the methylene group.[138]



17

The through-space interaction between the double bond and the aromatic fragment in benzobicyclo[2.2.2]octadienes [139] and dibenzobicyclo[2.2.2]octatrienes [140] has been studied by quantum chemistry and photoelectron spectroscopy. The results of the influence of substituents in the benzene ring of dibenzobicyclo[2.2.2]octatrienes **18** on the stereoselectivity of epoxidation are shown in Table 1.[140]



It was found that electron-withdrawing substituents (NO_2, F) facilitate the *syn*-attack, whereas electron-donating substituents do not exert this type of influence.

Table 1. Ratio of the *syn*- and *anti*-isomers in the products of electrophilic oxidation of 2-substituted dibenzobicyclo[2.2.2]octatrienes **18**.

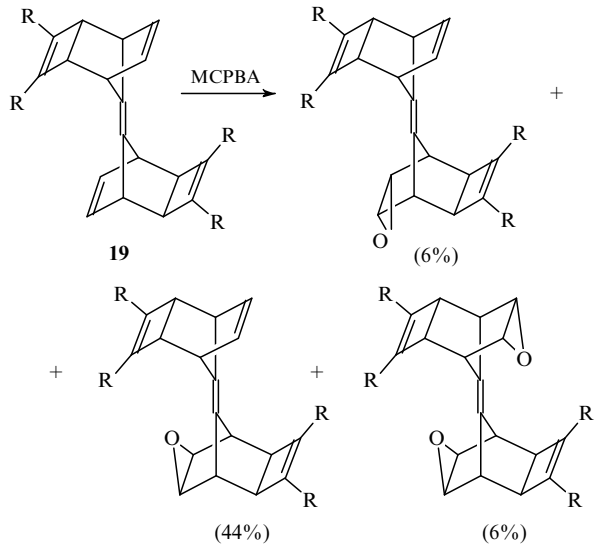
Oxidant	Substituent X	Yield (%)	Ratio *syn* : *anti*
MCPBA	H	88	50 : 50
	NO_2	46	77 : 23
	OMe	63	48 : 52
	F	86	58 : 42
OsO_4	H	90	50 : 50
	NO_2	67	85 : 15
	OMe	96	48 : 52
	F	96	68 : 32
$KMnO_4$	H	58	50 : 50
	NO_2	48	88 : 12

Gandolfi *et al.*[141] have found that the 80% – 96% *syn*-stereoselectivity of the attack by MCPBA on the double bond of *endo*,*exo*-5,6-disubstituted bicyclo[2.2.0]oct-2-enes (containing OAc, CN, *etc*. as substituents) is controlled by hyperconjugation of the σ*-orbitals of the bonds being formed with antiperiplanar σ-bonds of the allylic fragments.

In studies of epoxidation of anhydrides, nitriles, and esters of the norbornene series,[142 – 145] it has been found that these compounds undergo only the *exo*-attack by peroxy acids. The reported formation of *endo*-epoxides on treatment of 5-substituted norbornenes with *O*-benzylmonoperoxycarbonic acid [6] seems doubtful; apparently, in this case, too, *exo*-epoxidation occurs.[146]

exo-Stereoselective epoxidation has also been observed for the 7-oxa analogues of substituted norbornenes,[147 – 150] for bicyclic nitrogen-containing systems with a similar structure,[151] and for a broad range of bis-adducts of cyclopentadiene with various dienophiles.[152] The *exo*-stereoselectivity of the Prileschajew reaction is strictly observed for unsaturated propellanes related to norbornene. For complex polyenes (for example, for the com-

pound **19**), stereoselectivity is retained, together with the chemoselectivity of the attack at the double bond.[153]

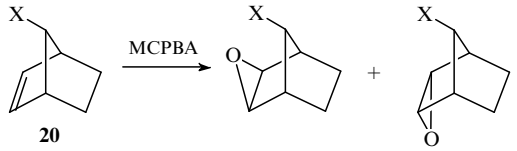


According to the known Bartlett, Lynch, and Pausacker scheme,[17] it can be assumed that formation of the transition state in the epoxidation of substituted norbornenes faces difficulties if the *exo*-area of the norbornene fragment contains bulky groups belonging to any of the two reacting molecules. The influence of methyl groups in various positions of the norbornene fragment on the stetreochemistry of epoxidation by MCPBA has been estimated quantitatively (Table 2).[30, 154, 155] It can be seen from Table 2 that only the *syn*-Me group at the 7-position prevents the attack. These data are consistent with the results obtained earlier for epoxidation of bornylene. For example, the formation of a mixture of isoborneol, borneol, epiisoborneol, and epiborneol[156, 157] upon the reduction of bornylene epoxide proves unambiguously the presence of a mixture of stereoisomers of the epoxide, the quantitative composition of the resulting mixture of alcohols being indicative of predominant *endo*-attack in epoxidation.

Table 2. Influence of the position of methyl groups on the stereochemistry of epoxidation of substituted norbornenes.

Compound	Epoxide yield (%)	Content of *exo*-isomer (%)
Norbornene	87	99.0
7,7-Dimethylnorbornene	87	6.0
1-Methylnorbornene	88	99.0
2-Methylnorbornene	100	99.5
1,7,7-Trimethylnorbornene	80	5.0

To estimate the influence of the size of various groups on the stereochemistry of epoxidation, epoxidation of *syn*-7-substituted norbornenes by MCPBA was carried out[158, 159] (Table 3).



X = H, Cl, $SnMe_3$, Br, Me, Bu^t.

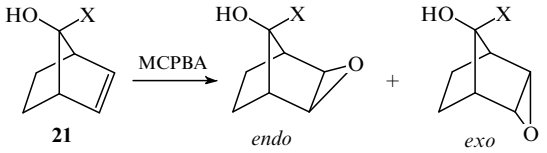
It can be seen from Table 3 that neither the van der Waals radius nor the length of the C–X bond are crucial for the efficiency of the *endo*-attack. The found *exo* : *endo* ratios vary in parallel with the size of the 'open space' between the double bond and the substituent, calculated by Davis *et al.*[159] by the procedure

Table 3. Influence of the character of substituents on the stereochemistry of epoxidation of substituted norbornenes **20**.

Substituent X	Content of *exo*-isomer (%)	*exo* : *endo*	C–X bond length /Å	Van der Waals radius of the substituent /Å
H	99.0–99.5	100	1.10	1.20
Cl	62.0	1.6	1.77	1.80
$SnMe_3$	55.0	1.2	(2.18)	–
Br	45.0	0.8	1.94	1.95
Me	6.0–14.0	0.1	1.54	2.00
Bu^t	0.0	0.0	(1.54)	–

proposed by Wilcox.[160] Any influence of the polar factor can be ruled out because the outcomes of the epoxidation and hydroboration reactions are identical.

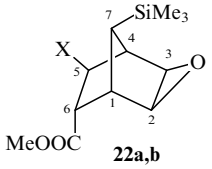
Gassman *et al.*[161] showed that methyl and nitrile groups have different effects on epoxidation of the double bond in substituted *anti*-bicyclo[2.2.1]hept-2-en-7-ols **21**.



X = Me (*exo* : *endo* = 22 : 78), CN (*exo* : *endo* = 45 : 55).

Epoxidation of 7,7-dibromomethylnorbornene yielded the isomers in approximately equal amounts.[162]

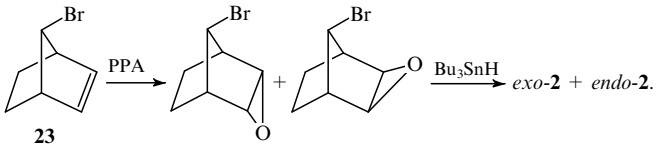
The data presented above[161, 162] disprove the results obtained in another study[163] in which the products **22a**,**b** obtained by epoxidation of substituted norbornenes with a *syn*-7-trimethylsilyl group were identified as containing an *exo*-epoxide ring.



X = H(**a**), COOMe (**b**).

In the light of the data available from the literature, the *exo*-attack by a peroxy acid seems relatively unlikely. Moreover, the ^1H NMR spectral parameters reported by Fleming and Michael[163] unambiguously point to the *endo*-configuration of the epoxide ring. In fact, the H(2) and H(3) protons are responsible for chemical shifts of 3.63 and 3.53 ppm (**22a**) and 3.62 ppm (**22b**). The chemical shifts of the corresponding protons in *syn*-7-bromo(chloro or trimethylstannyl)-*exo*-2,3-epoxybicyclo[2.2.1]-heptanes are 3.24, 3.26, and 2.97 ppm, whereas those in the corresponding *endo*-epoxides are 3.67, 3.70, and 3.45 ppm.[158, 159]

The influence of steric hindrance on the epoxidation of *syn*-7-bromobicyclo[2.2.1]hept-2-ene **23** by peroxyphthalic acid (PPA) has been studied.[25] The stereoisomeric bromoepoxides formed in this reaction [mostly, the *endo*-isomer, 1.8 : 1] were subsequently reduced by tributyltinhydride at 140 °C.

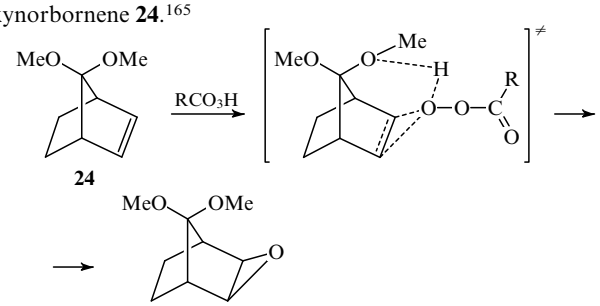


The resulting *endo*-2,3-epoxynorbornane **2** was studied by spectroscopy and by kinetic methods.

The *syn*-substituents at the 7-position, which are arranged in space close to the double bond, should certainly influence not only the direction but also the rate of epoxidation. The rates of the reactions of *anti*-7-*tert*-butylbicyclo[2.2.1]hept-2-ene, containing

the bulkiest *tert*-butyl group, with diimide, hydrogen, mercury acetate, and MCPBA are lower than the rates of the same reactions of norbornene by factors of 1.55, 3.77, 5.49, and 5.16, respectively.[164] Unfortunately, no data concerning epoxidation of the *tert*-butyl-substituted *syn*-isomer are presented in the study cited;[164] however, it does not enter into the complex-formation reaction with Ag^+ or reactions with diimide, mercury acetate, or benzenethiol even in the *endo*-direction. This might be due to the repulsion of the ethylene fragment from the *tert*-butyl group resulting in a distorted molecular geometry and hampered *endo*-attack.

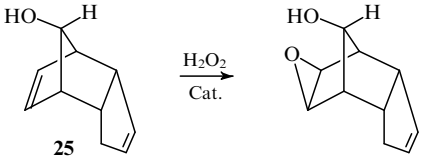
However, in some cases, substituents in the bridge facilitate the *exo*-attack. This is possible when the polar factor proves to be more significant than steric strain, for example, for 7,7-dimethoxynorbornene **24**.[165]



24

In the opinion of the researchers cited,[165] the *exo*-addition is a consequence of formation of a hydrogen bond between the attacking peroxy acid and the oxygen of the 7-methoxy group.

The involvement of a hydroxy group in epoxidation is apparently a general reaction route. For instance, it accounts for the chemo- and stereo-selectivity of the oxidation of the alcohol **25** in the presence of a molybdenum catalyst[166] and also of other reactions.[167]



25

V. The influence of substituents in the bicyclic system of norbornene on the reactivity of the double bond towards peroxy acids

Only a few studies specially devoted to the kinetics of epoxidation of substituted norbornenes have been published. Thus Brown *et al.*[168] demonstrated that the steric effect of the 7,7-dimethyl substitution is manifested as the change in the orientation of the attack by the oxidant (MCPBA) and as a 100-fold decrease in the reaction rate compared with that observed for norbornene, *exo*-epoxidation being retarded by more than three orders of magnitude.

A kinetic study dealing with epoxidation of 5,6-disubstituted (Cl, Br, COOMe) norbornene derivatives by perbenzoic acid (PBA) has been published.[169] The rate constants for this reaction, which correlate with the Hammett constants increase slightly in the following series of isomers: 5,6-*exo*-*cis* < 5,6-*trans* < 5,6-*endo*-*cis*. The researchers believe that these substituents exert mainly a polar influence, the effect of *exo*-substituents being stronger.

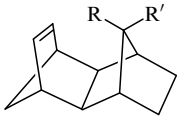
The crucial role of the inductive effect has been found for epoxidation of stereoisomeric norborn-2-ene-5-carboxylic acids and their esters.[1, 142, 144, 145] According to the kinetic studies of Berti *et al.*,[144] the possibility of an influence of the carboxyl group on the rate-determining step of this reaction can be ruled out, because the ratio of the reaction rates for the *endo*-acid and its ester proved to be similar to that found for *ortho*-stilbenecarboxylic acids and their esters. The situation changes dramatically in those cases where the substituent assists the reaction, as has been observed for epoxidation of norbornene derivatives containing *endo*-5-hydroxymethyl and *endo*-carboxamide groups.[1, 144, 145, 170, 171] In both cases, intramolecular rear attack by the nucleophilic group on the electrophilic centre in the intermediate 'alkene – peroxy acid' complex results in cyclisation. Epoxidation of the corresponding *exo*-stereoisomers follows the normal pathway.[172–174] (see also Section VII).

The influence of solvation and specific interactions has been clearly demonstrated in relation to epoxidation by peracetic acid of a number of stereoisomeric nitriles, acids, esters, amides, and alcohols, and also *endo*-stereoisomeric nitro- and bromomethyl-derivatives of norbornene.[154] In the presence of functional groups possessing clear-cut proton-donor or proton-acceptor properties, the inductive influence of substituents is masked by solvation effects; this has an influence on the correlation of the rate constants with the Taft constants of substituents. The effects of carboxyl and carboxamide groups on the epoxidation depend substantially on their orientation; in *exo*-isomers these groups are 'open' to the formation of intermolecular hydrogen bonds, whereas in *endo*-isomers they are shielded by the carbon cage of the molecule.

Quantum-chemical PM3 calculations for a number of transition states formed during epoxidation of substituted norbornenes by performic acid and comparison of the calculated parameters with the results of kinetic studies made it possible to find a correlation between the logarithms of the rate constants ($\lg k$) and the calculated activation enthalpies ($\Delta H^{\neq}$).[105]

Comparison of the results of correlation analyses of substituted norbornenes and propenes (the ρ constants for these reaction series at 40 °C are −0.446 and −1.31, respectively) implies that epoxidation of bicyclic alkenes is less sensitive to the inductive effect of substituents, because the bicyclic system smoothes out its influence.[175]

Kinetic data concerning the interaction of the π-bond with closely arranged groups in polycyclic systems related to norbornene can be found in several studies. The through-space interaction has been studied in relation to epoxidation of substituted propellanes **26a – f**.

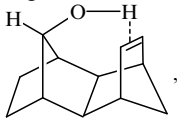


26a – f

a: R = R′ = H;
b: R = H, R′ = OH;
c: R + R′ = O;
d: R = OH, R′ = H;
e: R = OMe, R′ = H;
f: R = H, R′ = OMe.

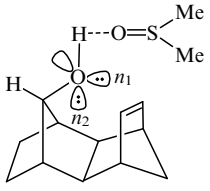
These reactions are *exo*-stereoselective in all cases; the reactivity of the double bond decreases in the following sequence (the relative epoxidation rates are given in parentheses): **26e** (13.20) > **26a** (1.00) > **26f** (0.36) > **26c** (0.04).[176, 177]

Analysis of the IR spectra recorded in weakly polar solutions proves that the compound **26d** contains a strong intramolecular hydrogen bond



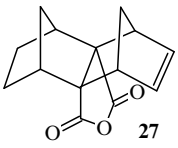
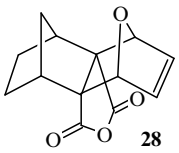
26d

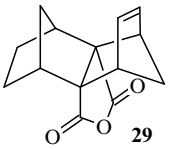
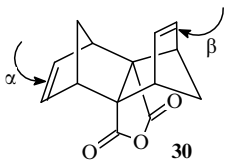
which deactivates the double bond. In aprotic bipolar solvents, the OH group participates in the formation of an intermolecular H bond with a solvent molecule.

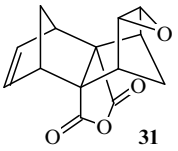
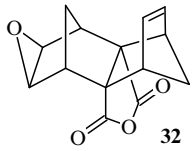


The through-space $n_1-\pi$ orbial interaction arising in the latter case increases the nucleophilic properties of the double bond. The same is true for the *syn*-methoxy group in **26e**. The reactivity of the ester **26e** is 340 times higher than the reactivity of the ketone **26c** in which this type of interaction does not occur.

Comparison of the relative rates of epoxidation by MCPBA of the double bonds in 1,4,5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalenes (**27**–**32**), incorporating an anhydride group, indicates that the *syn*-arrangement of this group largely passivates the double bond. Comparison of the rates of epoxidation of the compound **27** and its oxa-analogue **28** shows that in the presence of the oxygen bridge, the nucleophilicity of the double bond further decreases.[130]

Compound	 **27**	 **28**
Relative epoxidation rate	1.00	0.58

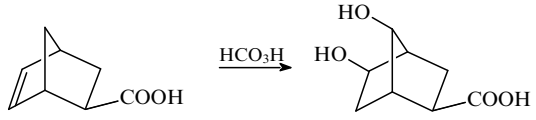
Compound	 **29**	 **30**
Relative epoxidation rate	19.00	1.20(α), 9.00(β)

Compound	 **31**	 **32**
Relative epoxidation rate	0.40	8.30

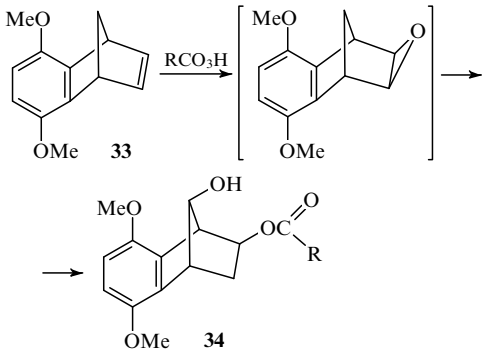
VI. Molecular rearrangements during epoxidation of norbornene

A peculiar feature of the epoxidation of norbornene derivatives is the formation of various isomeric products including those resulting from the Wagner–Meerwein rearrangement and hydride shifts.[178]

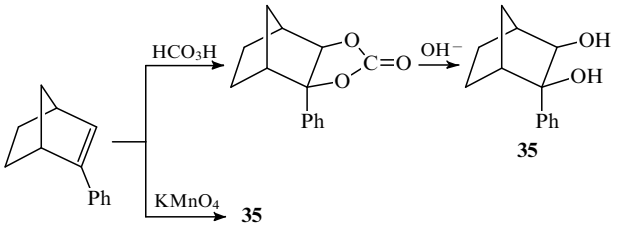
Electron-withdrawing groups at the 5- and 6-positions of the norborn-2-ene molecule prevent the C(1)–C(6) and C(4)–C(5) σ-bonds from participation in the delocalisation of charge at the C(2) and C(3) atoms; this decreases the role of nucleophilic assistance and, hence, the amount of rearranged products formed falls. For example, treatment of *exo*-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid[179] and its 7-oxa analogue[180] with performic acid gives rise to the corresponding *exo*-epoxy acids. Trifluoroperoxyacetic acid can also be used as the oxidant in this reaction. When the molecule contains only one *exo*-carboxyl group, the reaction with performic acid is accompanied *in situ* by the Wagner–Meerwein rearrangement.[144]



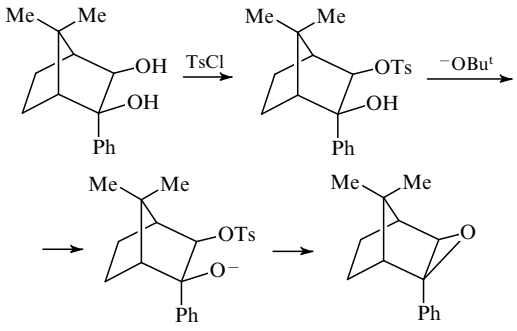
Electron-donating groups at the 5- and 6-positions increase the probability of the rearrangement during epoxidation; the rearrangement occurs even in those cases where one might expect the 'normal' reaction pattern. Thus, unlike benzonorbornene, epoxidation of which by various peroxy acids follows the normal route, the corresponding dimethoxy-derivative **33** reacts with trifluoroperoxyacetic or peracetic acid giving rise to the rearranged product **34**.



The addition of sodium acetate to peracetic acid makes it possible to retain some of the epoxide, whereas epoxidation by PBA gives the epoxide as the only reaction product.[181,182] Problems arise in those cases where the substituents at the double bond are capable of stabilising the carbocationic centre. These groups facilitate molecular rearrangements. For example, the Wagner–Meerwein rearrangement accompanies epoxidation of 2-phenylnorbornene with MCPBA[183,184] and 2-(*p*-anisyl)norbornene with peracetic acid even when a buffer solution has been added. Treatment of 2-phenylnorbornene with performic acid affords carbonate, due to the formation of a phenonium ion; hydrolysis of the carbonate results in the formation of *cis*-1,2-diol **35**. The latter can also be obtained from the same alkene using the Wagner method.[185]



Nevertheless, aryl-containing epoxides were successfully obtained by using peroxybenzimidic acid as the oxidant in a weakly alkaline medium.[186] It was also found that *exo*- and *endo*-2,3-epoxy-2-phenylbornanes can be synthesised from the corresponding *cis-exo*- and *cis-endo*-diols.[185]

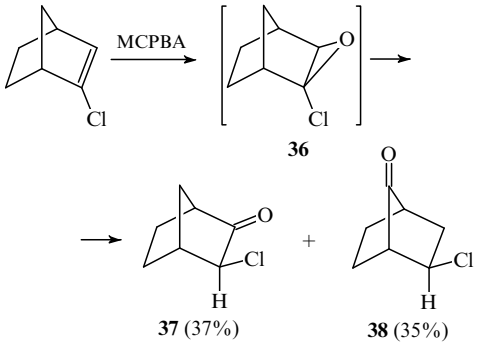


Stereoisomeric 2-methoxy-2,3-epoxynorbornanes have been prepared in a similar way.[158]

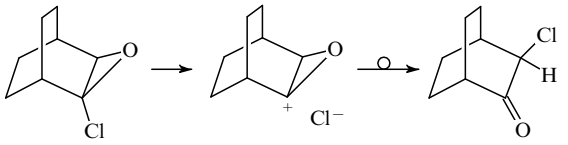
Later, diaryl-substituted oxiranes of the norbornene series have been synthesised from the corresponding diols on treatment with triphenylphosphine or other reagents.[187]

Chlorine atoms at the double bond of norbornene exert a similar influence. Epoxidation of 2-chloro- and 2,3-dichloronorborn-2-ene by MCPBA yields extremely unstable epoxides.[188–190]

Thus epoxide **36** decomposes at room temperature with heat evolution giving rise to a mixture of nine bicyclic compounds, ketones **37** and **38** being formed as the major products.



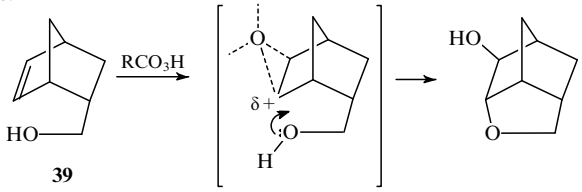
Oxidation of optically active (−)-(*R*)-2-chloronorbornene provided evidence indicating that the rearrangement involves a chloride shift rather than a hydride shift and that isomerisation is intramolecular. Unlike the epoxide **36**, 2,3-epoxy-2-chlorobicyclo[2.2.2]octane isomerises only at 100 °C in a sealed tube giving 3-chlorobicyclo[2.2.2]octan-2-one and no Wagner–Meerwein rearrangement products.[73]



Aliphatic and alicyclic α-chloroepoxides behave in a similar way.

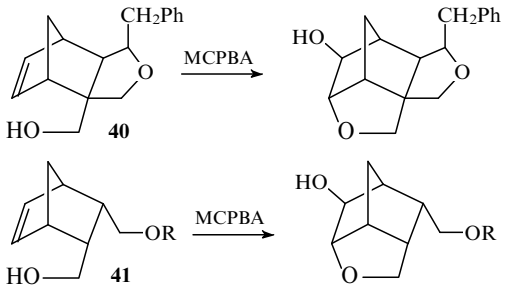
VII. Intramolecular cyclisation in reactions of substituted norbornenes with peroxy acids

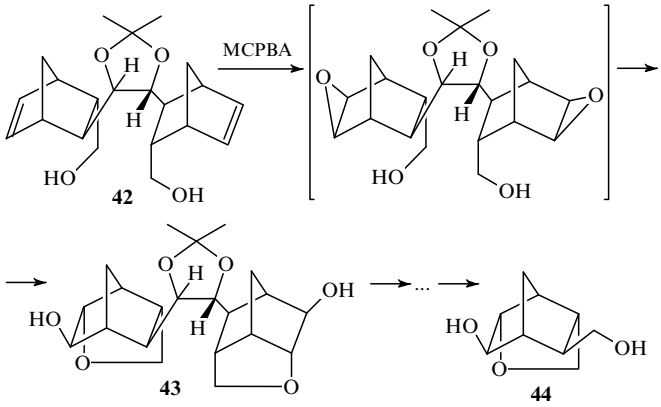
Electrophilic intramolecular cyclisation of alkenes is a well-known reaction.[191] Whereas epoxidation of acyclic alkenes is rarely accompanied by cyclisation, for substituted norbornenes reactions of this type are quite common.[4] Nucleophilic groups, for example, a hydroxy group, present in the rear *endo*-area are often involved in epoxidation giving rise to cyclisation products.[145, 192, 193]



This is due to the favourable arrangement of the nucleophile in the area of antibonding π*-molecular orbital of the epoxide ring being formed. In accordance with the Kerten–Hammett principle, the possibility of realisation of molecular conformations, convenient for the formation of activated complexes, is especially significant in this case.

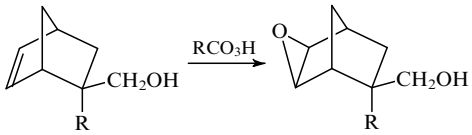
It is noteworthy that alcohol **39** reacts with perbenzoic acid forty times faster than the corresponding acetate.[144] Oxidation of norbornenes **40**–**42** follows a similar pathway.[194–197]



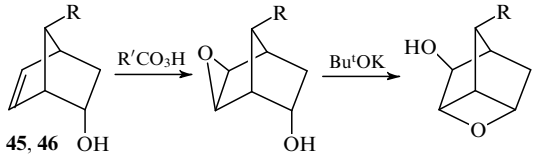


Bis-ether **43** is an intermediate in the synthesis of natural loganin **44**.[198]

Epoxidation of *exo*-hydroxymethyl substituted stereoisomers proceeds in a traditional way.[145]

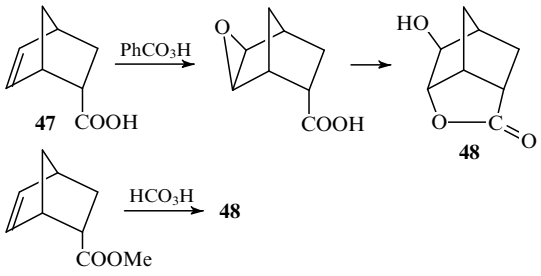


The hydroxy group in *endo*-5-hydroxynorborn-2-enes **45a**,**b** does not participate in cyclisation.[145] Shibasaki *et al.*[199] and, later, Holton and Kennedy[200] have converted the alcohols **45a**,**b** into stable epoxy alcohols, which have been subsequently converted into various cyclised and rearranged products by treatment with potassium *tert*-butoxide in tetrahydrofuran.

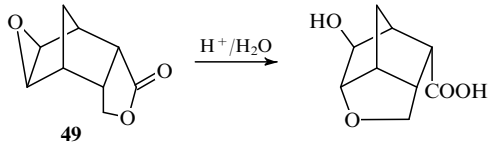


R = H (**45**), OCH_2Ph (**46**).

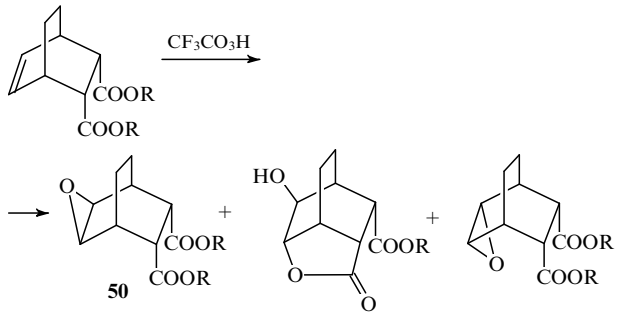
Epoxidation of acids of the norbornene series differs from that of alcohols in that in this case, the resulting epoxide intermediates are relatively stable. Thus, according to the data of IR spectroscopy, oxidation of acid **47** by perbenzoic acid yields initially an epoxy acid, which rapidly isomerises into hydroxy lactone **48**.[144]



The lactone **48** can also be obtained from methyl 5-norbornenecarboxylate by treating it with performic acid. Treatment with other peroxy acids results in the conventional transformation of this ester into the epoxide.[1,6] The different reactivity of hydroxymethyl and carboxyl groups towards cleavage of the oxirane fragment is reflected in the pattern of hydrolysis of epoxy lactone **49**.[201]

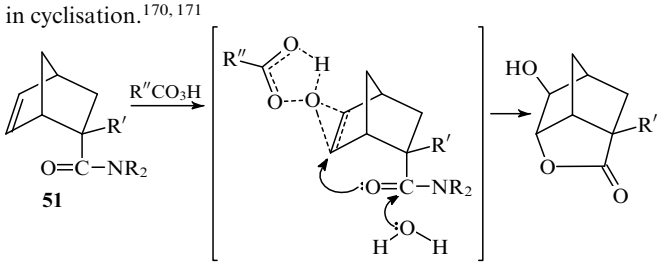


It has been shown[142,202] that epoxidation of dicarboxylic acids of the norbornene series is accompanied by lactonisation, if at least one of the carboxyl groups occupies an *endo*-position. Unlike substituted norbornenes, *endo*-acids and esters of the bicyclo[2.2.2]octene series are converted under similar conditions into mixtures of *exo*- and *endo*-epoxides and lactones; judging from the results of a special study,[138] the latter are produced only from *exo*-epoxides **50**.



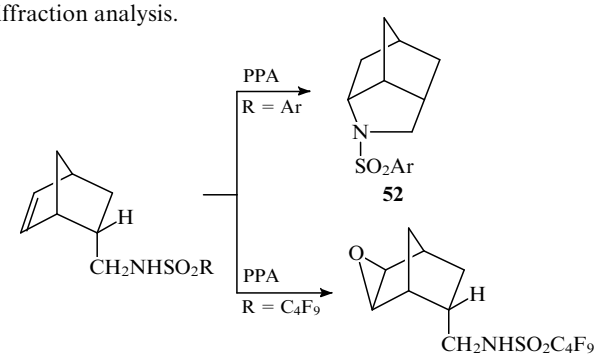
Comparison of the behaviour of the two related bicyclic systems reveals two substantial points distinguishing bicyclo-[2.2.0]octenes from substituted norbornenes, namely, the absence of *exo*-stereospecificity in the attack by a peroxy acid and a decrease in the ability to form lactones. Apparently, this is due to different degrees of strain and to specific conformational features of these systems.

It has been reported that the amide group can also participate in cyclisation.[170,171]

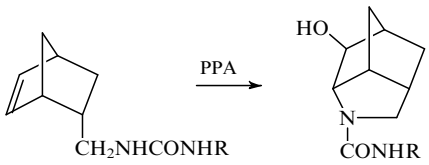


Lactonisation of *endo*-carboxamides **51** (R = Alk, Ar, H; R′ = Me_3N) occurs apparently *via* intramolecular rear attack by the carbonyl oxygen on the electrophilic centre in the intermediate 'alkene–peroxy acid' complex or in the intermediate compound. The corresponding *exo*-stereoisomers are readily converted into epoxides.[173,174]

The formation of similar heterocyclic derivatives containing other heteroatoms has been little studied. Formation of epoxide from unsaturated sulfone has been reported.[203] The attempt to obtain nitrogen-containing products of cyclisation from norbornenedicarboxamides failed.[204] In 1994, substituted 4-azatricyclo[4.2.1.0^{3,7}]nonanes **53** (azabrendanes) were prepared by treatment of *endo*-(*N*-arylsulfonyl)bicyclo[2.2.1]hept-2-en-5-ylmethylamines with peroxyphthalic acid.[205,206] The structure of the polycyclic cage of azabrendanes was confirmed by X-ray diffraction analysis.



Later, it was shown that the decrease in the basicity of the nitrogen atom following the replacement of the arylsulfonamide group by perfluoroalkylsulfonamide group prevents intramolecular cyclisation.[207] However, in the case of similar reactions of *endo*-ureas, substituted azabrendanes were isolated.[208]

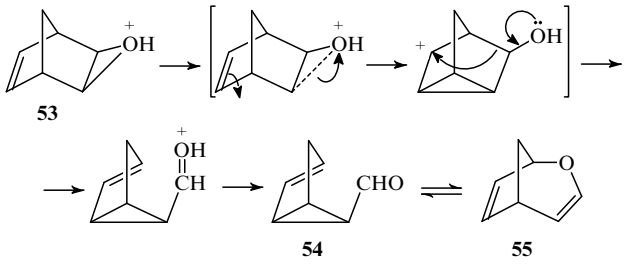


exo-Stereoisomeric derivatives readily form epoxides under similar conditions.[205–210]

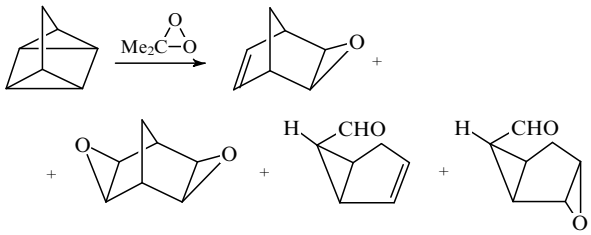
VIII. Epoxidation of diene systems incorporating norbornene or related fragments

In the case of a favourable arrangement of the double bonds in a molecule of bicyclic diene, π-bonds may be involved in epoxidation, instead of σ-bonds which normally participate in transformations of norbornene; this should increase the probability of the *endo*-attack by a peroxy acid. In fact, the products of epoxidation of norbornadiene by perbenzoic, monoperoxyphthalic, or peroxyacetimidic acid were found to contain 13% of *endo*-epoxynorbornene.[211] The stereoisomeric *endo*-epoxides synthesised from 7-methylnorbornadiene are stable upon refluxing in benzene containing traces of toluene-*p*-sulfonic acid.[212] The oxidation of 7-phenylnorbornadiene gives no *endo*-epoxide, which might be due to coordination of the peroxy acid to the electron-donating benzene ring.[212]

However, the major product of the oxidation of norbornadiene is *exo*-2,3-epoxynorborn-5-ene; the participation of a π-bond in the transformations precludes the traditional rearrangements (Wagner–Meerwein rearrangement, hydride shifts) and results in the formation of *endo*-bicyclo[3.1.0]hex-3-ene-6-carbaldehyde **54** in equilibrium with cyclic ether **55**.[213,214] The transformation thus discovered is referred to as the Meinwald rearrangement. The different behaviour of the stereoisomeric *exo*- and *endo*-epoxides demonstrates the importance of a favourable arrangement of the frontier orbitals for donor–acceptor interactions to occur. These π–π* interactions reflect the general type of behaviour of norbornadiene in electrophilic reactions.

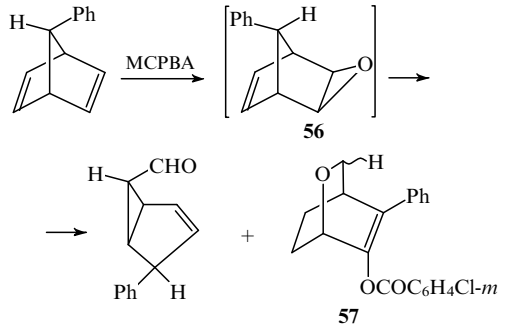


It should be noted that oxidation of norbornadiene with dimethyldioxirane yields both mono- and diepoxide;[215] the starting norbornadiene was prepared *in situ* by isomerisation of quadricyclene.

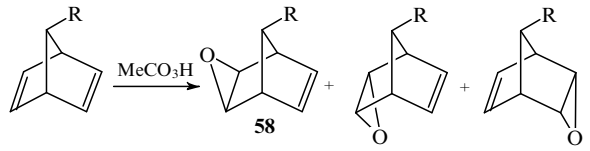


The rearrangement to bicyclic aldehydes induced by peroxy acids is also typical of *exo*-epoxides formed from 7-methyl- and 7-phenyl-norbornadiene;[212] in the latter case, the main reaction product **56** undergoes epoxidation followed by cleavage of the

epoxide ring with rearrangement and by cyclisation being thus converted into side product **57**.

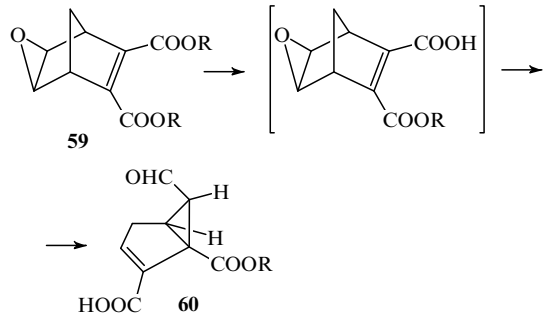


This rearrangement was used to prepare an intermediate compound in the synthesis of prostaglandins. Thus *exo*-epoxide **58** resulting from oxidation of 7-alkenylnorbornadiene (80%) was used in subsequent transformations.[216]



R = CH=CH—C(OSiMe$_2$Bu^t)(C$_5$H$_{11}$)H

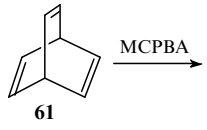
Apart from the labile epoxides with alkyl substituents described above, their quite stable analogues **59** with electron-withdrawing alkoxycarbonyl groups at the double bond are also known.[217] However, acid esters prepared *in situ* by enzymic hydrolysis of symmetrical diesters immediately undergo the Meinwald rearrangement giving bicyclo[3.1.0]hex-2-ene derivatives **60** in nearly quantitative yields.[217]

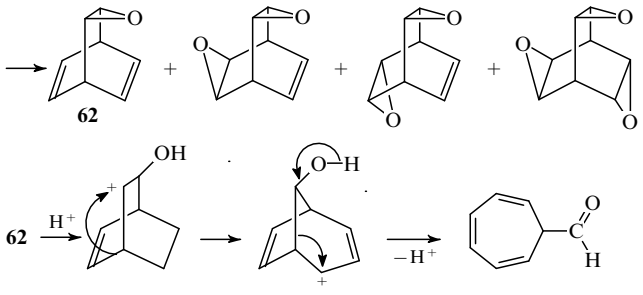


R = Me, Et, Pr^n.

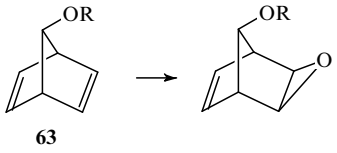
The stability of the epoxides can be increased by introducing additional electron-withdrawing fragments. In fact, the 7-oxa-analogue of the epoxide **59** was prepared in a quantitative yield and used successfully in the synthesis of the nucleoside antibiotic cordycepin.[218]

As opposed to norbornadienes, the less strained bicyclo-[2.2.2]octadiene, on treatment with perbenzoic acid, adds only one equivalent of the acid, the addition occurring from the less shielded *endo*-side, which is richer in electrons.[219] When an excess of the peroxy acid was used, stable diepoxide was obtained. Based on barrelene **61**, mono-, di-, and tri-epoxides have been obtained.[220] They can be isolated but are easily transformed in acidic media. Thus monoepoxide **62** is easily converted into cycloheptatriene-7-carbaldehyde.[220]

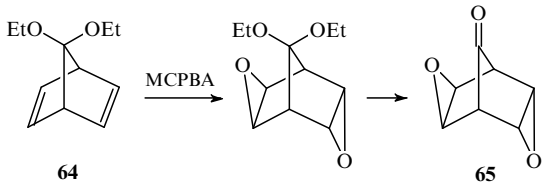




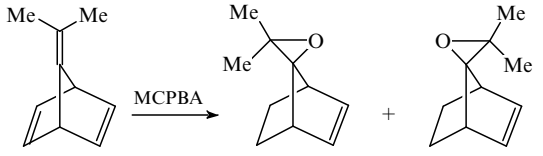
Oxidation of 7-alkoxynorbornadienes **63** occurs through *exo*-attack by a peroxy acid. Even in the case of 7-*tert*-butoxy-substituted derivative, despite the obvious steric hindrance, the reaction involves the *syn*-double bond.[122]



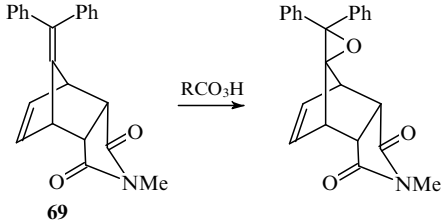
However, a study has been published, which casts doubt upon the amazing electronic influence of the *tert*-butoxy group.[221] In fact, it was found that in the case of 7,7-diethoxynorbornadiene **64**, both multiple bonds undergo epoxidation. The structure of diepoxyketone **65** was reliably confirmed by NMR spectroscopy; however, the order of introduction of the epoxide fragments has not been studied in this work.[222]

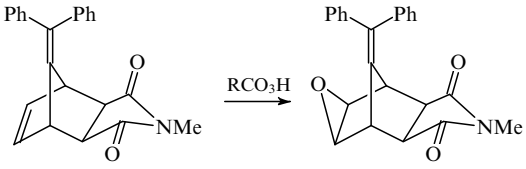


In recent years, considerable attention has been devoted to epoxidation of dienes of the norbornene series containing exocyclic double bonds. It was shown that treatment of 7-isopropylidenenorbornene **66** with an equimolar amount of MCPBA results in selective epoxidation of the exocyclic double bond, the ratio of products **67** and **68** being equal to 34 : 66, due to the preferential *anti*-attack.[139, 223]



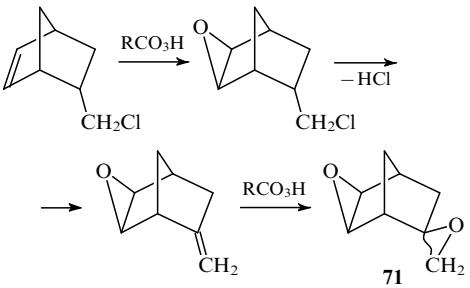
A similar picture has also been observed for 9-isopropylidenebenzonorbornenes; the introduction of chlorine or fluorine atoms into the aromatic ring facilitates formation of the *syn*-product. Epoxidation of stereoisomeric 7,7-diphenylmethylene-*N*-methylnorbornene-2,3-dicarboximides **69** and **70** demonstrated that the stereochemistry of the dicarboximide group has crucial influence on the direction of the process.[224]





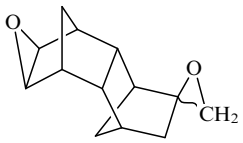
70

Epoxidation of 5-chloromethylnorborn-2-ene to give diepoxide **71** is described in a patent.[225]



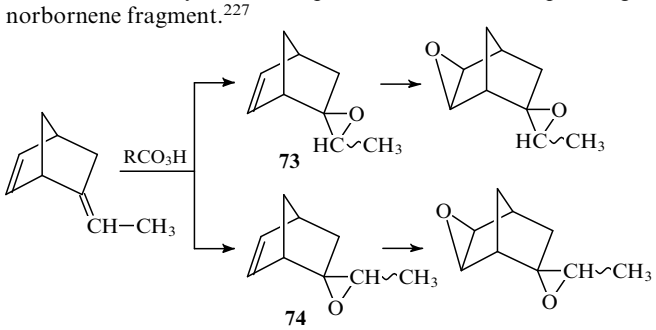
71

Later, the product **71** and its tetracyclic analogue **72** were obtained from the adducts of cyclopentadiene with allyl chloride (or bromide).[226]



72

In recent years, particular attention has been devoted to epoxidation of available vinyl- and ethylidenenorbornenes and the dimer of cyclopentadiene. Vinyl- and ethylidenenorbornenes have been oxidised by peracetic, peroxyphthalic, *m*-chloro- and *p*-nitro-peroxybenzoic, and peroxyimidic acids. Earlier, it has been noted that vinylnorbornene can be oxidised to give the monoepoxide by oxygen in the presence of nitropalladium complexes.[126, 227, 228] When ethylidenenorbornene is epoxidised by peracetic acid, the ratio of the products of oxidation at the endo- and exo-cyclic double bonds, found by ^{1}H NMR spectroscopy, is equal to 1 : 6.[228] When equimolar amounts of the reactants are used, the reaction yields monoepoxides **73** and **74** incorporating a norbornene fragment.[227]

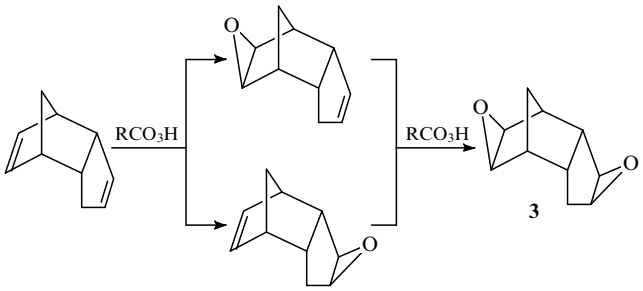


The monoepoxide **73** obtained using peroxyphthalic acid isomerises to give *endo*-5-acetylbicyclo[2.2.1]hept-2-ene. The different behaviour of the isomers is indicated by the fact that reactions of the diene with the above peroxy acids result in different ratios of the monoepoxides. Further epoxidation of the monoepoxides **73** and **74** affords stereoisomeric diepoxides.[227]

As the double bond moves away from the norbornene fragment, their mutual influence becomes less significant and the double bond in the ring becomes more reactive. Voronenkov *et al.*[229] found that the logarithms of the rate constants for epoxidation are correlated with the first vertical ionisation potentials for a broad range of dienes of this type.

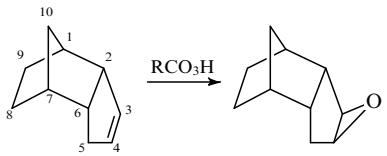
Numerous studies have been devoted to epoxidation of the cyclopentadiene dimer (CPDD) containing double bonds in the norbornene fragment and in the five-membered ring. The interest aroused by this object is due both to its accessibility and to the valuable properties of various polymeric materials based on epoxide derivatives of CPDD.[230] Oxidation is usually carried out by peracetic,[231, 232] peroxyphthalic,[230, 233–235] and monoperoxymaleic [236, 237] acids (both free peroxy acids and those obtained *in situ* from the corresponding anhydrides and hydrogen peroxide have been used).[233, 236]

The high sensitivity of the norbornene system in the transition state to steric effects results in that, of the four possible stereoisomers, only one product **3**, characterised by the *exo*-arrangement of both epoxide fragments, is produced. When the oxidant is in deficit, a mixture of monoepoxides is formed, the substituted epoxynorbornane being the major product.[238, 239] The ratio of the monoepoxides depends substantially on the oxidant used.[64]

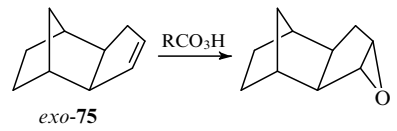


3

It is of interest that during epoxidation of *endo*-tricyclo-[5.2.1.0 ^{2,6}]dec-3-ene **75**, the attack occurs from the side of the methylene bridge, whereas the *exo*-isomer is attacked from the opposite side.

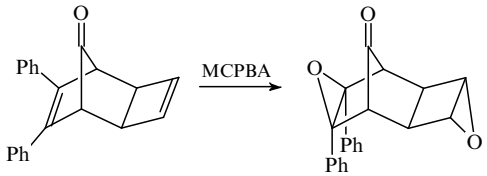


endo-**75**

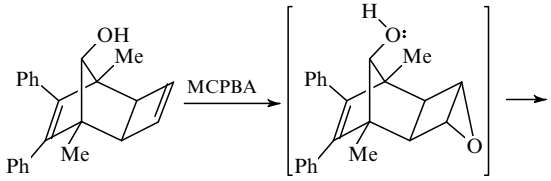


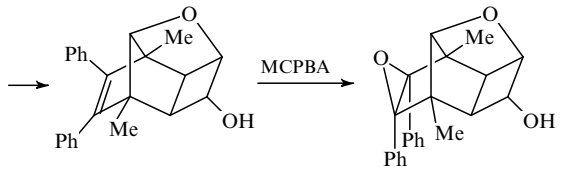
exo-**75**

An attack by a peroxy acid from the *endo*-area has also been observed for polycyclic systems with a cyclobutene fragment.[240]

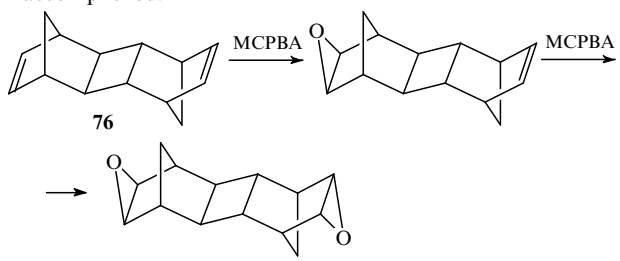


The oxidation of the corresponding alcohol occurs chemoselectively only at the cyclobutene fragment and is accompanied by intramolecular cyclisation.

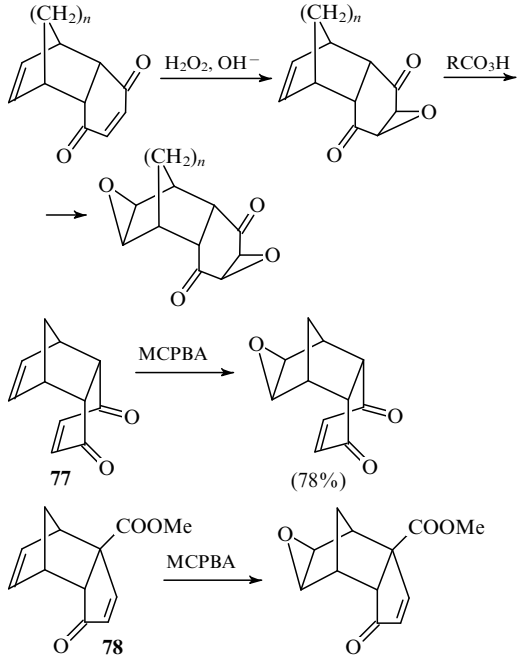




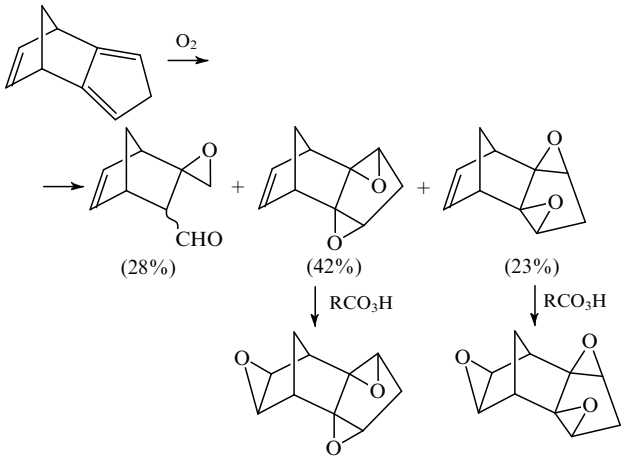
Mono- and di-epoxidation of the norbornadiene dimer **76** has been accomplished.[129]



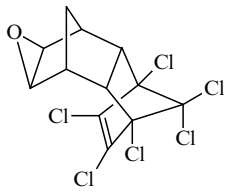
The double bonds can be epoxidised successively or selectively; in particular, this occurs for the adducts of cyclic dienes with benzoquinone and their analogues ($n = 1, 2$).[241]

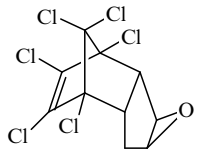


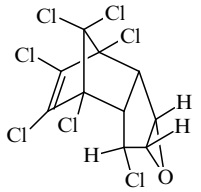
The first stage of interaction of the diene **77** with peroxy acids is complicated by side processes,[242] whereas electrophilic epoxidation of the diene **78** occurs smoothly.[243] Consecutive oxidation of a triene system has been described.[244]



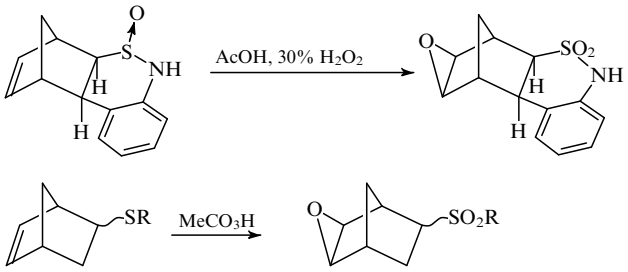
Electron-withdrawing substituents decrease the nucleophilicity of the double bond in the bicycloheptane fragment of the norbornene and cyclopentadiene dimers; this results in selective epoxidation of the double bonds in the diene fragment. The syntheses of dieldrin (**79**), endrin (**80**), and other epoxides can serve as typical examples.[194, 245, 246] In the case of heptachloro-derivative **81**, the oxirane fragment is *endo*-oriented.[247]



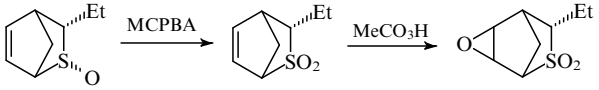




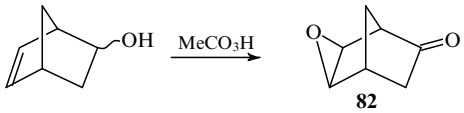
Of special interest are non-chemoselective reactions in which other fragments of the molecule are oxidised in parallel with the double bond.[248–250]



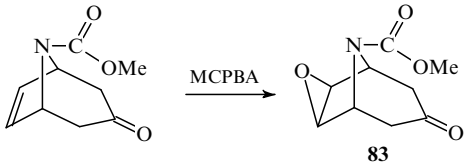
However, by choosing appropriate peroxy acids and reaction conditions, one can attain a high degree of selectivity of the oxidation.[251]



It should be noted that the epoxide **82** prepared from hydroxynorbornene cannot be obtained by epoxidation of the corresponding unsaturated ketone, because the double bond is deactivated by the electron-withdrawing carbonyl group, and the latter is selectively attacked by the peroxy acid.[252]



When the carbonyl group is located far from the double bond, stable epoxy ketones can be prepared, in particular, ketone **83**, which is a precursor of alkaloids of the tropane series.[151]



In most cases, epoxidation of ketones and alcohols is carried out with protected carbonyl or hydroxy groups, because the

epoxide derivatives of substituted norbornenes are especially unstable in the presence of acids.[218, 251]

IX. Conclusion

In this review, the known methods for epoxidation of substituted norbornenes and dienes incorporating a norbornene fragment are described and diverse transformations accompanying epoxidation, in particular, molecular rearrangements, which often end with the formation of new heterocyclic systems, are considered. The information presented here demonstrates that norbornene and its derivatives occupy a special place in the chemistry of epoxidation of cycloalkenes. This is due to special structural features and to the strained character of the carbon cage, which predetermines the possibility of chemo- and stereoselective transformations during the oxidation of these compounds.

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