Translated from *Uspekhi Khimii*, **54**, 1674-1705 (1985) U.D.C. 547.422.127

Advances in the Development of Methods for the Epoxidation of Olefins

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Data obtained in recent years on the epoxidising agents and the mechanism of their interaction with olefins are surveyed. Different types of hydroperoxides as well as certain short-lived epoxidising intermediates of the molecular and radical types functioning *in situ* are examined.
The results of the stereospecific epoxidation of aliphatic and alicyclic compounds using the directing influence of functional groups (OH, COOH, R, SiR_3, etc.) are presented.
The bibliography includes 225 references.

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I. INTRODUCTION

In terms of the character of the behaviour of the reagent and the substrate, the epoxidation of olefins has much in common with a whole series of reactions regarded as models of biological monoxygenation[1]—the oxidation of amines, phosphines, sulphides, Schiff bases, azo-compounds,[2-4] arenes,[5] alkanes,[6] etc. For this reason, new information about the synthesis and mechanism of action of any of the epoxidising agents acquires general theoretical importance for the development of ideas about liquid-phase oxidation as a method of organic chemistry and for the understanding of many biological processes.

The chemistry of oxiran has developed in two directions. One of these involves the industrial manufacture of the practically most important epoxy-compounds: the oxides of ethylene, propene, but-1-ene, butadiene, styrene, epichlorohydrin, and a wide assortment of aliphatic cyclic mono- and di-epoxy-compounds produced on a small scale.[2-7] The second direction is associated with the important role of oxirans in the living processes of the plant and animal world. Properties of epoxidised terpenoids, carotenoids, and steroids,[2] the juvenile hormonal activities of many natural and synthetic epoxy-compounds,[8-10] and the toxic and carcinolytic properties of epoxide-containing intermediates, formed in the oxidation of aromatic hydrocarbons,[11] have been widely investigated.

The physiological activity of many natural compounds containing epoxide oxygen has led to the problem of the development of the synthesis of their analogues and of a wide set of methods for stereospecific and regiospecific epoxidation. Considerable advances have been achieved in this field,[12] using on a wide scale the directing influence of neighbouring functional groups (OH, COOH, SiR, etc.). In its turn, the discovery of the stereochemical consequences of epoxidation has become a powerful means for the elucidation of the mechanism of the oxidation of various objects.

The aim of the present reivew was to give a systematic account of epoxidising agents and to elucidate the common features and differences in the mechanisms of their formation and action on olefins†.

The central place in the review is occupied by the expoxidation of olefins by peracids, which is the reaction most fully investigated in close association with solvation and association phenomena. The importance of data obtained in this connection is determined by the fact that many reactions involving hydroperoxides proceed, like the Prilezhaeva reaction, in a complex system of donor–acceptor interactions and combine both heterolytic and homolytic processes.

II. ORGANIC PERACIDS

Since the publication in 1974 of Prilezhaeva's fundamental monograph,[2] considerable progress has been achieved in the development of the methods of epoxidation by peracids. The methods for the synthesis of anhydrous peracids, in the first place the lower (C_1–C_4) peracids, based on the acylation of hydrogen peroxide by carboxylic acids or anhydrides in the presence of acid catalysts, have attracted constant interest.[13-16] Aqueous peracetic acid has acquired industrial importance.[17] Polymeric peracids have been synthesised by the interaction of carboxylated polystyrene with hydrogen peroxide in methanesulphonic acid.[18]

Crystalline perbenzoic acid is obtained by an improved method from benzoyl chloride[19] and by the alkaline hydrolysis of benzoyl peroxide.[20] Many olefins have been epoxidised by perbenzoic acid and its ring-substituted analogues at the instant of formation from the corresponding acid chloride and potassium peroxide in the presence of an interphase transfer catalyst.[21,22]

†A systematic consideration of the mechanism of the epoxidation of olefins by oxygen is outside the framework of this review.

m-Chloroperbenzoic acid is widely used for the synthesis of oxirans, which are sensitive to acids, in the presence of buffers (aqueous solutions of Na_2CO_3, $NaHCO_3$, Na_2HPO_4).[23-27]

There has been a continuation of studies on the synthesis of peracids by the oxidation with atmospheric oxygen of aldehydes: acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde,[28-30] *p*-toluic aldehyde,[31] pentafluorobenzaldehyde,[32] *p*-methoxycarbonylbenzaldehyde.[33]

Monopermaleic,[34-38] mono-, di-, and tri-chloroperacetic,[34-41] and 2,4-dinitroperbenzoic acids[42] have been used successfully for the epoxidation of electron-deficient olefins. The catalytic influence of organic nitrogen-containing bases (amines, pyridine, urea, guanidine, etc.) and inorganic bases on the reaction of acid anhydrides with peroxides has been demonstrated.[37,43-46] The method used in the employment of perphthalic acid has been improved.[47-49] Perphthalic acid *in situ* and in the crystalline form[47,50-52] as well as *p*-methoxycarbonylperbenzoic acid[33] are oxidants which are promising in practice. The epoxidising capacity of many peracids can be deduced from the relative rates of epoxidation of allyl bromide by peracetic, performic, monochloroperacetic, perbenzoic, monoperphthalic, and monopermaleic acids at 40 °C in acetic acid, which are respectively 1.0, 1.54, 1.70, 1.84, 8.7, and 15.1.[48]

The rate constants for the epoxidation of 1,4-dibromo-2-methylbut-2-ene with monochloroperacetic (at 10 °C) and dichloro-, trichloro-, and trifluoro-peracetic (at 2 °C) acids are in the ratios 1 : 13 : 1000 : 2700, although the differences between the overall efficiencies of these acids are not so significant. Furthermore, trichloroperacetic acid is more effective than its fluorine-containing analogue, since the enhancement of the electron-accepting influence of the substituents entails a decrease of the equilibrium concentration of peracid in the reaction of acid anhydrides with hydrogen peroxide, while the losses of active oxygen owing to decomposition increase.[45]

The most important application of peracids is epoxidation of electron-deficient olefins, which requires concentrated solutions of peracids, in many cases with added buffering bases. A series of studies have therefore been carried out on the mechanism of the interaction of peracids with olefins over a wide range of reactant concentrations and acid–base properties of the medium.[48,53-56] It was found that in multicomponent solutions with strong complex formation via hydrogen bonding the interaction of an olefin with a peracid proceeds as a complex process, the kinetics and direction of which depend to a high extent on the proton-donating and proton-accepting properties of the medium. Many of the experimental facts established under these conditions cannot be accounted for by the mechanism adopted, which presupposes the involvement in the reaction only of the unsolvated peracid molecule with an intramolecular hydrogen bond.[2]

It is striking that the epoxidation of the olefin proper competes as a rule with the spontaneous or olefin-induced decomposition of peracids. On the other hand, when the conditions are altered, the olefin can suppress the spontaneous decomposition of the peracid.[53-56] It has been shown by kinetic methods that the intermediate olefin–peracid complex disproportionates in many cases into isomerisation or epoxide ring-opening products, bypassing the oxiran formation stage.[57] The influence of solvation of the final result of the reaction has been demonstrated in relation to the epoxidation of diallyl maleate by permaleic acid in solvents of similar basicity: diethyl ether and tetrahydrofuran (THF).[58] Many oxirans are formed in the former case, while the epoxide ring opening products are formed in THF.

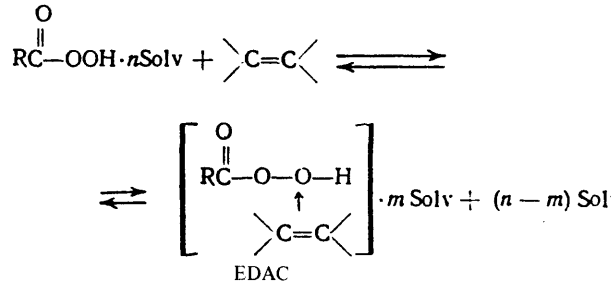
Experiments[54,66] on the epoxidation of olefins by peracids under the conditions of a gradual increase of the initial concentration of the base (dimethylformamide (DMF) in solution, which is known[59] to entail a change in the structure of the associated peracid species, are extremely instructive. Initially an increase of the DMF concentration reduces k_{epox}, as was to be expected,[2] and subsequently, in a rigorously defined range of its concentrations, the homolytic olefin-induced decomposition of acids is observed. Finally, the region of the induced decomposition is rapidly replaced by the region of the inhibition of the spontaneous decomposition of RCO_3H. The epoxidation constant k then increases significantly, although the degree of association of the peracid with the base increases.

The induction and inhibition of the decomposition of peracids by olefins depend specifically and to a large extent on the conditions governing solvation and association with the bases.[56] Purified peracids (95–99%) also decompose extremely vigorously under the influence of an olefin and, with increase of the concentration, the contribution of the decomposition process increases.

The epoxidation reaction and the accompanying reactions of peracids undergo autocatalysis or inhibition[55,56] up to the complete cessation of the reaction in the presence of still considerable concentrations of the reactants in solution.[60] The second order of the reaction is observed only at high acid concentrations, for example, when peracids synthesised from acid anhydrides are used. Under these conditions, the acid and oxiran (a base) formed in the reaction do not alter significantly the acid–base properties of the medium.

The so-called dilution effect is characteristic of the Prilezhaev reaction and the competing processes:[55,56,60,61] with decrease of the concentration of the reactants and following the dissociation of intermolecular hydrogen bonds, the specific rate (k) diminishes and the activation parameters (E_{act}, $\Delta S^{\neq}$) vary within wide limits. In many cases a kind of "organic" version of the salt effect is observed: an artificial increase of the concentration of associated species of the type of $RCO_2^-.BH$ increases the rate of the process,[56,60,62] which indicates an appreciable charge separation in the activated complexes.

It follows from the above that the olefin attacks the peracid incorporated in a system of intermolecular bonds. The donor–acceptor ("soft") interaction of the reactants competes with the "hard" complex formation reaction of the peracid via hydrogen bonding and, as a result of the substitution of the ligands, the solvent, or the base (Solv) in the solvation shell, the olefin produces a new association complex, a π-complex or an electron donor–acceptor complex (EDAC):



EDAC

The EDAC concentration is comparable to those of the reactant and, when present in a sufficient excess, the olefin is capable of fully solvating the peracid by accelerating the epoxidation process so that it is several times faster.[56,63-65]

The EDAC formation stage is responsible for the autocatalysis and inhibition of the epoxidation reaction. The autocatalysis is caused by the fact that the acid formed in the

reaction promotes the desolvation of the peracid, as a result of which the equilibrium in the formation of EDAC is constantly shifted to the right, controlling the rate of reaction as a whole. The autocatalysis may be manifested also as a consequence of the rapid increase of the molar ratio [olefin]/[RCO_3H] during the reaction.[56] The inhibition of the epoxidation can occur in its turn when the peracid is involved in complex formation with the oxiran as a base via hydrogen bonding (in the presence of highly pure, 95–99%, peracids) or with associated species with the type $RCO_2^-.\overset{+}{B}H$.[60] An increase of the excess of the olefin relative to RCO_3H and an increase of temperature weaken the inhibiting effect of the bases and their associated species.

Thus the rate and direction of the Prilezhaev reaction are determined by the nature of the peracid associated species. Many spectroscopic studies[61,66–69] and quantum-chemical calculations[2,69–72] have been devoted to the establishment of their structure. It is known that in inert solvents at low temperatures peracids form monomers with a weak intramolecular hydrogen bond, while in concentrated solutions they produced dimers.[2,66,67] The barrier to rotation about the O–O bond is insignificant (1.00–4.00 kcal mol^{-1}).[68–70] The available information about the geometry of the monomers is not unambiguous. According to the results of certain quantum-chemical calculations,[2,70] the peracid molecule is planar. However, it has been established that the *p* electron of the neighbouring nitrogen and oxygen atoms in the molecules of hydrazine, hydrogen peroxide, and many peroxy-compounds[68,73] tend to leave the energetically unfavourable eclipsed position (the *gauche*-effect).

The displacement of the *p* electrons of the external peroxide oxygen atom from the conjugation plane of the *p* and π electrons of the R–C(=O)–O– unit in the peracid molecule is reflected in the fact that, in terms of its proton activity, it is greatly inferior (by 3.5 orders of magnitude) to the related normal acid.[2,68] These ideas agree with the calculation of dipole moments of RCO_3H by Swern and co-workers[74] (the dihedral angle θ between the COO and OOH planes is 72°) and also with quantum-chemical calculations[70,71] (θ = 40–60°). It has been noted that the *s-trans*-conformation is just as characteristic of peractic acid as the *s-cis*-conformation.[72] The *s-trans*-structure has been attributed to *o*-nitroperbenzoic and perpelargoric acids (θ = 146°) on the basis of X-ray diffraction analysis.[70]

Calculation has shown[69] that the $RCO_3H.RCO_2H$ associated species is much more stable than the dimer $RCO_3H.RCO_3H$ and that not only the carbonyl[71] but also the peroxide oxygen atom, linked to the >C=O group, can function as the proton acceptor in the formation of the latter dimer.

Experimental and calculated data make it possible to infer that the peracid molecule can exist in both *syn*-chelated and transoid forms. It must be assumed that in solutions the conformation of RCO_3H is influenced significantly by the nucleophilic effects of the solvent, the reagent, and other components on the acid proton and the peroxide oxygen atom.

The infrared spectra of dilute solutions of peracids show that in basic solvents (dioxan, THF, etc.) the free RCO_3H monomer is virtually absent—the ν(OH) band undergoes a 70–90 cm^{-1} bathochromic shift.[67–69] The ^1H NMR spectra of solutions of *m*-chloroperbenzoic (85%) and perlauric (99.5%) acids in the concentration range 0.2–2 M also lead to the conclusion that in a basic medium the peracid is wholly solvated, although the degree of proton transfer to the solvent varies within a wide range.[61,69] At a sufficiently high concentration, ensuring the emergence of the peracid molecule from the solvent cage, the signal of the protons becomes narrow and intense, which indicates their equivalence, attained as a consequence of the rapid exchange in the chain of hydrogen bonds. Acid admixtures appreciably accelerate the formation of associated chain species.

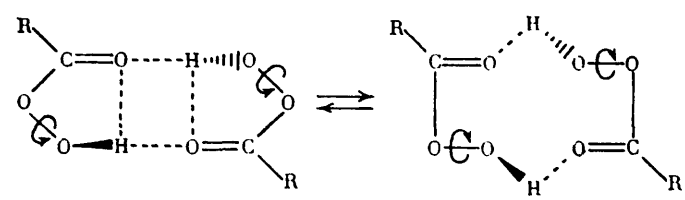
Spectroscopic data and the general theoretical ideas about the acid–base interactions in organic media[60] permit the conclusion that the state of the solutions of peracids, containing admixtures of acids and bases, is characterised by a multiplicity of different types of associated species, differing in the degree of proton transfer to the base (B) or the conjugate base (A), although, within certain concentration ranges and for certain ratios of the acid and basic components, specific dominant forms of the associated species are produced.

Using the "from the structure of the peracid to the mechanism" principle[2] as a guide, the probable mechanisms of the interactions of olefins with peracids can be represented as follows.

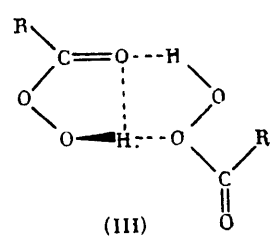
In inert solvents, at low concentrations of the peracid, which exists mainly in the monomeric form, the Bartlett–Lynch mechanism probably operates.[2] However, the character of the proton transfer remains obscure. Thus dilution of the solution with pure (99%) peracid, which leads to the dissociation of the intermolecular hydrogen bonds, reduces the k_{eff} for the epoxidation reaction, although it was to be expected that an increase of the fraction of the monomer would have the opposite influence. The rate constants for the epoxidation of hex-1-ene in benzene (1 M, 30 °C) at perlauric acid concentrations of 1.5 and 0.5 M are 1.15×10^{-4} and 0.84×10^{-4} litre mol^{-1} s^{-1} respectively. Thus, even a weak intermolecular interaction between the peracid monomers and dimers exerts an appreciable electrophilic cooperative effect on the elimination of the acid anion.

The preferred migration of the proton in the "olefin–peracid" transition state to the "internal" peroxide and not the carbonyl oxygen atom has been demonstrated by calculation.[75]

Peracid dimers appear in solution with increase of concentration. The combination of cisoid and transoid conformers leads to the following possible structures:

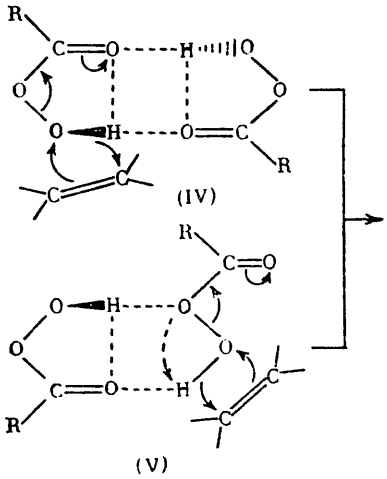


(I) (II)



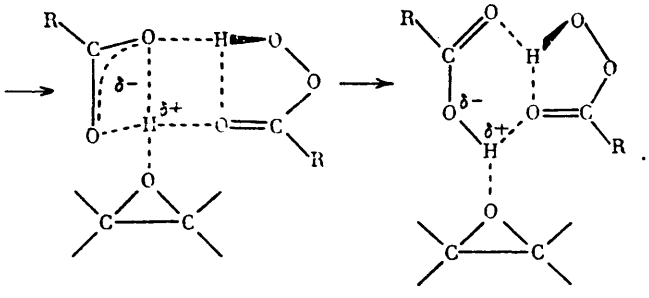
(III)

The formation of dimers promotes the epoxidation reaction—k_{eff} increases:



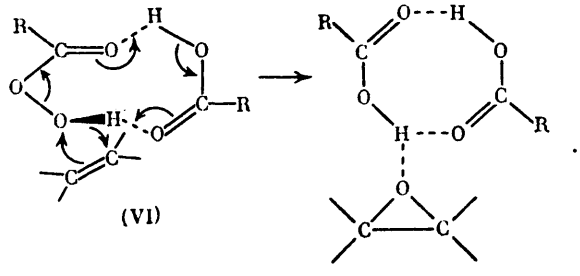
(IV)

(V)



The dimeric form II is less favourable in the epoxidation reaction, since the approach of the olefin to the external peroxide oxygen is blocked by the second peracid molecule.

In the presence of acids, associated species of the type $RCO_3H.RCO_2H$ are formed together with the dimers RCO_2H. $.RCO_2H$, which appreciably accelerates the epoxidation reaction:

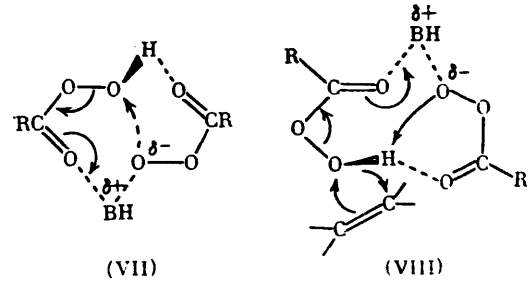


(VI)

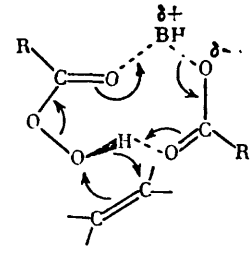
It can be seen, that in conformity with the minimum displacement principle,[76] only intermolecular proton transfer leads to the optimum structure of the acid dimer.

Small amounts of added base are inserted in the acid associated species without causing their complete decomposition#.[59] The base binds to the proton in the dimer (I) and promotes the transformation of the *s-cis*-conformers into the *s-trans*-conformers (VII) and permits the donor–acceptor interaction of the peroxide atoms and in the limiting case the decomposition of the peracid.[61]

#The associated species $RCO_2^-Na^+.RCOOH$ is known to be very stable.[77]



(VII) (VIII)

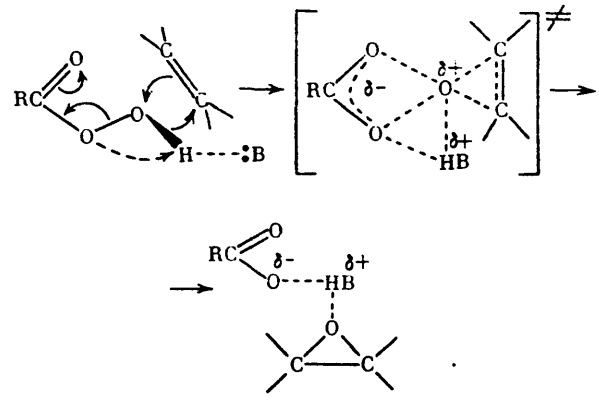


(IX)

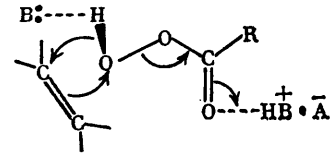
On the other hand, in the presence of an olefin, the epoxidation reaction behaves as the competing pathway (VIII). The epoxidation mechanism (IX) develops similarly when the base is incorporated in the associated species $RCO_3H.RCO_2H$.

The intramolecular migration of the proton in (VIII) and (IX) is less favourable than the intermolecular migration. In the intramolecular transfer in (VIII) the base would have been found to the weaker acid (RCO_3H) while in (IX) an anomalous acid dimer would have been formed.

At high concentrations of the base or after dilution with a basic solvent, the chelate complexes of the peracid decompose.[59] The peracid molecule linked to the base apparently exists, like peresters and acyl peroxides,[68,72] in the form of *s-trans*-conformers and proton transfer takes place in a solvent cage with participation of the conjugate base of the acid:



In the presence of large amounts of acids and bases, the relay proton transfer is most probable:



In the chelate complexes (VI), (VIII), and (IX) the non-coplanar attack on the olefin can induce the radical decomposition of the peracid with formation of carbon dioxide and an alcohol.

The data obtained in quantum-chemical and stereochemical studies of the π-complex and the "olefin–peracid" transition state[75] are fully consistent with the ideas described above, which were developed at a qualitative level. However, it has been stipulated that the attack by the peracid is directed to the carbon of the olefin double bond and not to the π-electron cloud.[78,79]

The study of the kinetics of the epoxidation of deuteriated styrene derivatives[79] established that the replacement of H by D in the α-position hardly influences the rate of reaction ($k_H/k_D = 0.99$), while deuteriation of the β-carbon atom leads to an appreciable isotope effect ($k_H/k_D = 0.82$). Since the secondary isotope effect is caused in the given instance by a change in the hybridisation of the carbon atom in the olefin double bond ($sp^2 \rightarrow sp^3$), the authors assume that only the formation of the C_β–O bond is manifested in the transition state. However, according to the proposed mechanism, the peracid functions as a nucleophile, which is consistent with the fairly well established fact that the peracid is electrophilic and the olefin nucleophilic.[2] One cannot rule out the possibility that the absence of an isotope effect in the deuteriation of the C_α atom is caused by the shielding influence of the bulky phenyl group.

For the interpretation of the structure of the "olefin–peracid" transition state (TS), it is useful to employ the idea that the elements of π- and σ-complex formation are combined in the structure of the protonated epoxide ring.[80,81] The reaction constant for the epoxidation of a number of olefins by a strong peracid, for example, monopermaleic acid,[56] is small in absolute magnitude ($\rho^* = -0.56$). According to the Bell–Evans–Polanyi principle, the nature of the transition state is in this case closer to that of the starting materials and the π-component predominates in its structure. The epoxidation by a weak peracid (peracetic acid)[56] is characterised by a high constant $\rho^* = -1.39$, the transition state resembles the final products, and the contribution of σ-complex formation increases. In terms of the molecular orbital (MO) method, the ring formation process is represented as a combination of the donor–acceptor overlapping of the bonding π_b orbital of the olefin with the σ^*_{O-O} orbital of the peracid and the dative interaction of the non-bonding orbital of the peroxide oxygen with the antibonding π^*_{antib} orbital of the olefin. The fact that the substituted propenes $CH_2{=}CH{-}CH_2{-}X$ (X = halogen or OR) are epoxidised with greater difficulty than the related 1,4-disubstituted but-2-enes, contrary to the hypothesis that the influence of the substituents is additive, can be accounted for from this standpoint.[82] The synchronous occurrence of the two types of orbital overlapping on formation of the oxiran ring apparently imposes definite requirements on the symmetry of the activated complex, as a result of which the asymmetrically substituted olefins are in a less favourable position.

In the alkaline epoxidation of polar multiple bonds, the sign of ρ^* changes[83] and the dative interaction becomes of decisive importance in the cyclisation stage.

Certain new stereochemical features of the reactions of olefins with peracids have been established, indicating that the rate of reaction and its direction are determined not only by electronic factors but also by the relaxation properties of the reactant molecules incorporated in the associated structure of the solution.

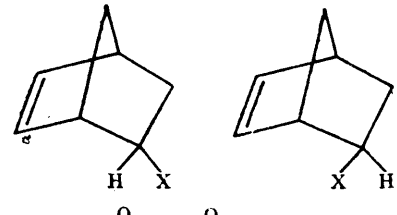
Previously it was believed[2,84] that the rate of reaction of the aliphatic compounds is independent of the steric influence of the substituents (especially alkyl substituents) at the reaction centre. However, it was found[85] that an alternative effect is characteristic of aliphatic reactants, namely the dependence of k_{eff} on the number of carbon atoms in the olefin (C_6–C_9) and the peracid (C_1–C_{12}) is represented by broken lines. Consequently, the alternating changes in the conformation of the R residue and of the molecule as a whole as the carbon chain grows can exert an unfavourable influence on the stage in which the reactants approach one another and are coordinated.

It is of interest to note that in a basic solvent (ethyl acetate) the long-chain RCO_3H proved to be unexpectedly more effective oxidants than the lower peracids (R = H or CH_3). This finding can be explained by the hydrophobic character of the massive alkyl component, which hinders the solvation of the peracid molecule. On the other hand, in an inert solvent (benzene), which does not solvate peracids, the strength of the latter is determined by the electronic factor: with increase of the bulk of R, the epoxidising capacity of RCO_3H diminishes.

Steric hindrance due to the increase in the size of the reactant molecules is observed also in other reaction series. Thus the loss of active oxygen in the epoxidation of allyl bromide by peracids in the series peracetic–perpropionic–perbutyric–perlauric increases owing to their induced decomposition[48] and the rate of epoxidation of the first olefin double bond in the diallyl esters of dicarboxylic acids $ROOC(CH_2)_nCOOR$ [58] increases only with increase of n from zero to two; subsequently k_{epox} diminishes.

The solvation of functional groups remote from the reaction centre has a significant influence on the rate of epoxidation.[58,82,86] Such solvation probably causes, by the increase of size, some loss of degrees of freedom by the reactant molecules and diminishes the probability of their effective collisions. In particular, it has been established that the rate of epoxidation (k_2) of the monoepoxides of the diallyl esters of dicarbocylic acids is much lower than the rate of formation (k_1) of the first epoxide ring ($k_1/k_2 = 4$).[58] When $n \geq 2$, this fact cannot be accounted for by the electron-accepting influence of the epoxide ring.

The decrease of the rate of epoxidation of the remote olefin double bond in sorbic acid esters[82] is caused by the increase in the size of the alcohol residue in the ester group. The character of the influence of the functional groups on the rate of epoxidation of the *exo*- and *endo*-isomers of substituted norbornanes is also determined by the solvation conditions:[86]



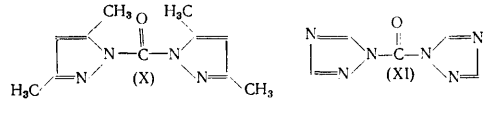
In the *exo*-position the substituents which tend to become involved in complex formation via hydrogen bonding (CO_2H, $CONH_2$) are "available" for the formation of intermolecular hydrogen bonds, while in the *endo*-position they are shielded by the carbon skeleton of the molecule. For this reason, the catalytic effect of the COOH group and the inhibiting influence of the basic $CONH_2$ group are manifested much more strongly in the *exo*-position. Certain nucleophilic groups ($CONH_2$, OH) in a series of *endo*-derivatives of norbornene exhibit an anchimeric cooperative effect on the epoxidation reaction.

III. HETEROANALOGUES OF PERACIDS

Derivatives of carbonic acid $X-\overset{\overset{O}{\|}}{C}-OOH$, where X represents nitrogen- or oxygen-containing functional groups, and the compounds $X-\overset{\overset{NR(H)}{\|}}{C}-OOH$ containing the azomethine group instead of the carbonyl group are close to organic peracids as regards their effectiveness. A characteristic feature of their chemical behaviour is an increased tendency towards decomposition[87,88] caused in the first place by the catalytic influence of the basic nitrogen-containing functional groups and rings[56,61] and in the second place the tendency towards decarboxylation of the monofunctional derivatives of carbonic acid, formed in the stage involving the transfer of active oxygen to the substrate. The decomposition of the heteroanalogues of peracids[87] leads to the formation of singlet oxygen, which is significant evidence for the heterolytic reaction mechanism and is consistent with the ideas developed by the present author.[56,61] The ability of the olefin to inhibit the decomposition reaction has also been noted.

Compounds of the above series are synthesised from hydrogen peroxide and the reaction concerned involves either nucleophilic substitution at the carbon atom of the carbonyl group or the nucleophilic addition to the azomethine or nitrile group.

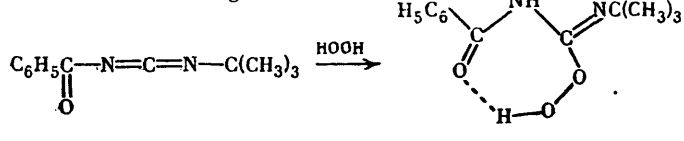
It has been noted that, in contrast to SeO_2, dialkyl carbonates and CO_2 do not form peracids in their reactions with H_2O_2, whereas peroxycarbamic acids, capable of epoxidising reactive alkenes of the type of cyclohexene, are formed from derivatives of dimethylpyrazole (X) and 1,2,4-triazole (XI):[87,88]



Among the hydroperoxy-derivatives of carbonic acid, mention should be made of *N*-benzoylperoxycarbamic acid ($C_6H_5-\overset{\overset{O}{\|}}{C}-NH\overset{\overset{O}{\|}}{C}-OOH$) and *O*-benzylperoxycarbonic,[89] and *O*-ethylperoxycarbonic acids[90,91] ($RO\overset{\overset{O}{\|}}{C}OOH$), obtained by treating hydrogen peroxide with benzoyl isocyanate ($C_6H_5\overset{\overset{O}{\|}}{C}-N=C=O$) in the first case and by compounds of the type $R-O-\overset{\overset{X}{\|}}{C}-X$, where R = $C_6H_5CH_2$ or C_2H_5 and X = Cl or $O\overset{\overset{O}{\|}}{C}CH_2C_6H_5$, in the last two cases.

The rates of epoxidation of *trans*-stilbene at 25 °C in benzene by *O*-benzylperoxycarbonic, perbenzoic, and *m*-chloroperbenzoic acids are in the ratios 7.12 : 4.27 : 15.0, while *N*-benzoylperoxycarbamic acid is 200 times more effective than perbenzoic acid, which is undoubtedly assisted by the possibility of the elimination of carbon dioxide from the "olefin–peracid" complex.

Carbodiimide is less reactive in the reaction with hydrogen peroxide than isocyanates and gives rise to peracid heteroanalogues only in the presence of electron-accepting substituents at the nitrogen atom:[87]



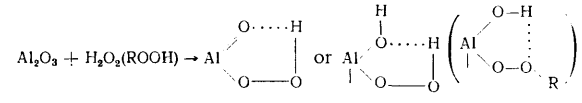
A similar peroxy-group is produced by cyanates ($RO-C\equiv N$),[87] benzonitrile,[92] and cyanamide ($H_2N-C\equiv N$),[93] which react with hydrogen peroxide via Paine's mechanism.[2] A method for the epoxidation of styrene by a mixture of acetonitrile and hydrogen peroxide in an alkaline medium with added Na_2HPO_4 has been proposed.[94]

A most powerful oxidant with the tentative structure $[(CH_3)_2\overset{+}{N}=CH-OOH]P\bar{O}_2Cl_2$, which epoxidises cyclenes at −80 °C, is formed in the H_2O_2–Vilsmeier reagent system.[95]

IV. INORGANIC PERACIDS

Inorganic peracids are employed as a rule at the instant of formation on treatment of the anhydrides (oxides), chlorides, and salts of acids with hydrogen or alkali metal peroxides. The possibility of their application is limited by the high acidity of the medium, which promotes the opening of the epoxide ring, and by the tendency towards decomposition, which increases in parallel with increasing strength of the peracids. A decrease of the pH of the medium is attained when acid salts are used. Naturally, the oxidising power of the hydroperoxide intermediate is then also lowered.

Vanadium, molybdenum, tungsten, selenium,[96–105] boron,[106] arsenic,[107] and aluminium[108] oxides have been used for epoxidation. They give rise to an epoxidising agent, for example:



The fact that the peracid and not hydrogen peroxide is involved in the epoxidation reaction has been confirmed by the kinetics of the oxidation of allyl bromide,[97] allyl alcohol,[98] and maleic and fumaric acids and their salts[99–103] by hydroperoxide derivatives of orthovanadic, tungstic, and molybdic acids. The above unsaturated acids are not oxidised by organic peracids.

Many derivatives of stilbene, chalcone, and acenaphthylene have been epoxidised by alkane- and arene-persulphonic acids,[21] obtained by the interaction of the corresponding chlorides ($C_6H_5SO_2Cl$, Cl_3CSO_2Cl, $CH_3C_6H_4SO_2Cl$, etc.) with potassium peroxide in the presence of a crown-ether as the phase-transfer catalyst. The broad spectrum of the activity of these reagents is probably due to the fact that they can function both in the undissociated state (RSO_2-OOH), executing an electrophilic attack on the multiple bond of, for example, stilbene, and in the form of the corresponding peroxide-anion (RSO_2-OO^-), which is capable of attacking the polar olefin double bond of the chalcone, like the hydroperoxide anion (HOO^-).

Peroxymonophosphoric acid epoxidises *trans*-stilbene but does not permit the isolation of cyclohexene, styrene, and α-methylstyrene oxides[109] because of the high acidity of the medium. It has been noted that the rates of epoxidation of *trans*-stilbene by H_3PO_5 and CH_3CO_3H are comparable, while the Baeyer–Villiger reaction is 100 times faster when perphosphoric acid is used. These differences are due to the fact that the rate-limiting stage in the oxidation of a ketone, namely the rearrangement of an acylhydroxyalkyl peroxide, is sensitive to acid catalysis, which is undoubtedly more effective in perphosphoric acid.

Benzeneperoxyseleninic acid has found application in the synthesis of epoxides.[96,110,111] Mixtures of areneseleninic acid ($X=C_6H_4Se\overset{\overset{O}{\|}}{}OH$, where X = NO_2, Cl, COOH, etc.) and

30–90% hydrogen peroxide epoxidise alkenes in the presence of phosphate buffer. The acid is used in catalytic amounts (0.5–5%).

It has been shown in relation to allyl alcohols and diolefins that a perseleninic acid is less stereoselective and regioselective than carboxylic peracids and alkyl hydroperoxides, which indicates its highly electrophilic nature.

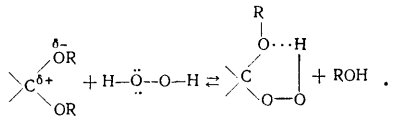
Presumably the replacement of the OH group by OOH in the acid reagent takes place also in the epoxidation of tetracyanoethylene with hydrogen peroxide containing added $HClO_4$.[112]

Triphenylsilyl hydroperoxide (Ph_3SiOOH) behaves like peracids in relation to olefins, ketones, and allyl alcohols,[109] although its structure is similar to that of alkyl hydroperoxides. The comparatively high epoxidising capacity of Ph_3SiO_2H is due to the dative interaction of the lone electron pairs of the neighbouring atoms (O, N, and halogen) and the unoccupied *d* orbitals of silicon, which is typical for silicon compounds.

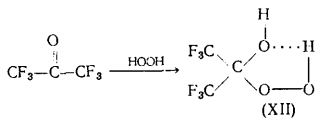
V. EPOXIDATION BY HYDROPEROXIDES ACTIVATED BY ELECTRON-ACCEPTING SUBSTITUENTS

The replacement of carbonyl oxygen in the peracid molecule by another, stronger electron acceptor (OH, OP, NP_2) leads to a series of hydroperoxides, which have lower oxidation potentials than peracids but do not lose their epoxidising capacity.

Rebek proposed a series of hydroperoxyethers,[87,113] obtained by the interaction of acetals, ketals, or orthoesters with 90% hydrogen peroxide, as epoxidising agents:



The products of the addition of hydrogen peroxide to the carbonyl group in ketones containing electron-accepting groups, namely tetrachloro-,[114] hexachloro- and hexafluoroacetones,[87,115,116] are more effective oxidants:



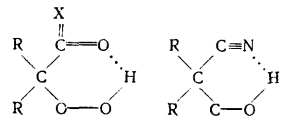
(XII)

The reagent (XII) epoxidises cyclic and acyclic olefins at 0 °C with a 60–93% yield of oxirans, while at an elevated temperature it oxidises ketones and esters.

A series of oxo-compounds (chloral, benzoin, acetophenone, acetoacetic ester, pentachlorobutanone, glucose, etc.) have been investigated in the epoxidation of cyclododecatriene and dicyclopentadiene.[117,118] It was found that the best results are achieved at 50–60 °C in the absence of a solvent. The rate of reaction is to a large extent determined by the diffusion constant. In particular, chloral generates the most reactive hydroperoxide, superior in its strength to the adduct of hexachloroacetone. Reagents of the above type make it possible to obtain monoepoxides in 25–95% yield virtually without an admixture of diepoxides.

The azomethine group in pyridinium salts and Schiff bases behaves similarly to the carbonyl group of ketones in the presence of hydrogen peroxide,[87] but the yield of oxirans is then low (3–45%).

The α-hydroperoxides of ketones, esters, nitriles, and amides,[119] formed in their autoxidation in the presence of potassium t-butoxide,[120] are epoxidising agents whose strength is comparable to that of peracetic acid:



X=OR, NR_2, R;
R=C_6H_5, CH_3

These reagents act stereospecifically on olefins—the *syn*-epoxyalcohol is formed preferentially in the epoxidation of 2-cyclohexanol. However, in contrast to peracids, the ester α-hydroperoxide oxidises *trans*-stilbene more easily than the *cis*-isomer, while *trans*-β-methylstyrene is oxidised more readily than cyclohexene. The selectivity of the reagent diminishes greatly when chloroform is replaced by benzene as the solvent.

The weak epoxidising capacity of the hydroperoxy-derivative of pyrazole, which is structurally similar to natural products, namely 4a-hydroperoxides of flavin, has been demonstrated.[121]

It is of interest to note the results of the oxidation of styrene by atmospheric oxygen on the styrene–oxygen copolymer as the template.[122,123] The dioxetan fragment of the copolymer

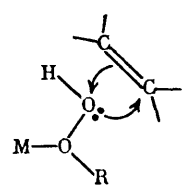


has been considered as the possible epoxidising group. An alternative version of the mechanism may involve epoxidation by the hydroperoxy-groups produced from the CH and CH_2 units in the α-position relative to the benzene ring or the peroxide bridge.

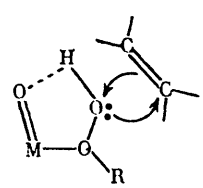
VI. HYDROPEROXIDE EPOXIDATION OF OLEFINS CATALYSED BY TRANSITION METALS

The state and principal trends in the development of the method have been fairly completely described in a monograph.[3] At the same time, it has been noted that the mechanism of the epoxidation of olefins by alkyl hydroperoxides and, in particular, the mechanism of the stage involving oxygen transfer to the substrate has not been ultimately elucidated.

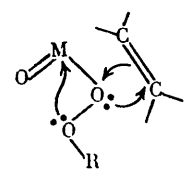
Most investigators have adopted mechanisms involving the formation of the complexes (XIII) and (XIV):[3,124]



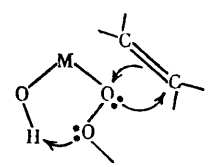
(XIII)



(XIV)



(XV)

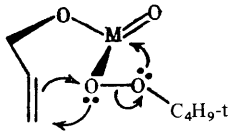


(XVI)

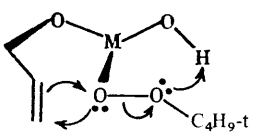
However, this is open to the objection that, according to the structures of compounds (XIII) and (XIV), the internal O(1) oxygen atom and not the more nucleophilic external O(2)

oxygen atom functions as the centre for the coordination with the catalyst in RO(1)O(2)H. This mechanism does not explain the exceptional reactivity of allyl alcohols.[125,126] Having examined the stereochemistry of the oxidation of the latter, Sharpless proposed mechanisms in which compounds (XV) and (XVI) are formed.[125,127] Preliminary experiments with the aid of tracer atoms showed that the ROOH molecule itself and not the peroxy-compound of the catalyst is involved in the stage responsible for the oxygen transfer.[128,129]

All the conditions for the simultaneous coordination of the catalyst to the peroxide oxygen and the allyl hydroxy-group exist in the complexes (XV) and (XVI), while in compounds (XIII) and (XIV) such interaction is ruled out on geometrical grounds:

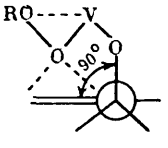


(XV)

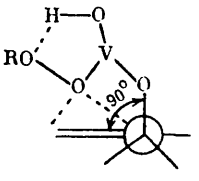


(XVI)

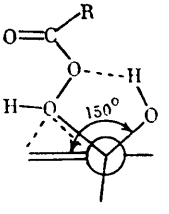
In their study of the stereochemical aspects of the epoxidation of cycloalkenols, Itoh et al.[126] determined the most probable geometry of the transition state when the alkyl hydroperoxides (XV) and (XVI) and the peracids (XVII) are used:



(XV)

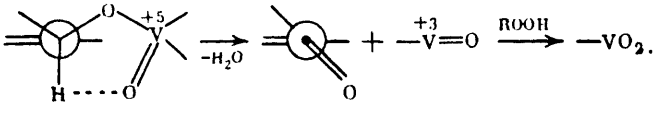


(XVI)



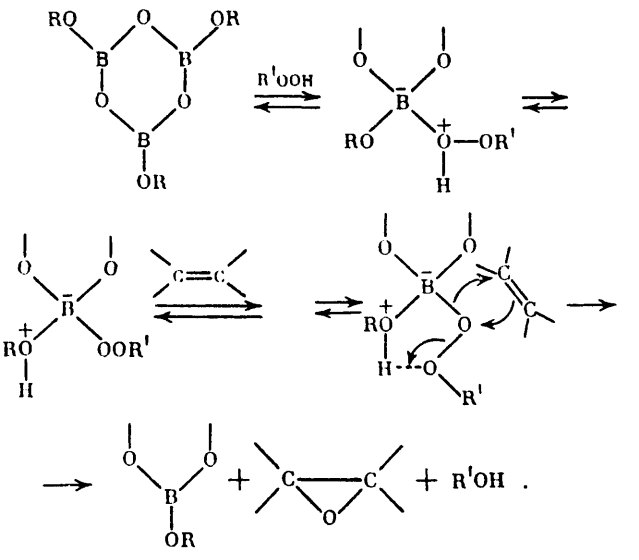
(XVII)

In the case of secondary allyl alcohols with a fixed conformation, which prevents formation of the complexes (XV) and (XVI) with a quasi-axial disposition of the OH group, the oxidation is by the oxygen of oxovanadium with subsequent regeneration of the oxidant by the hydroperoxide:

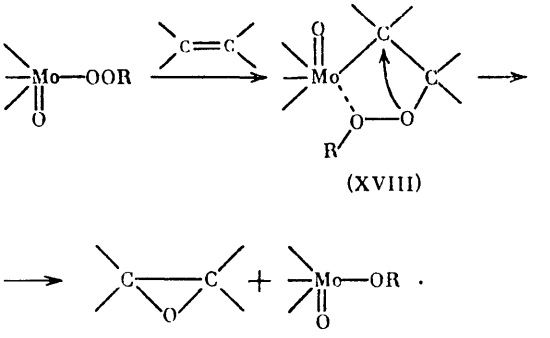


The ability of the metals employed in the oxidation reaction to form three-membered peroxy-compounds  [128,129] makes a shift of the central atom from the active oxygen to the alkoxide anion in compound (XV) entirely realistic. Under other acid–base conditions, the "proton" mechanism (XVI), corresponding to the idea of nucleophilic substitution at the peroxide oxygen atom, may be preferable.[55] The relative contributions of the mechanisms (XV) and (XVI) are apparently determined by the ratio of the oxo- and hydroxylated forms of the catalyst.

In the light of the ideas described concerning the role of aprotic and protic acids, epoxidation in the presence of borates[130] can proceed as follows in the peroxide oxygen transfer stage:

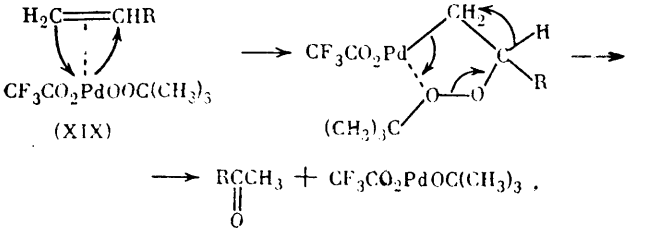


A mechanism has been proposed for the hydroperoxide epoxidation with formation of a five-membered metal peroxide complex (XVIII):[131]



(XVIII)

The above mechanism is based on the analogy with the oxidation of terminal alkenes to methyl ketones by peroxy-compounds of palladium (XIX):



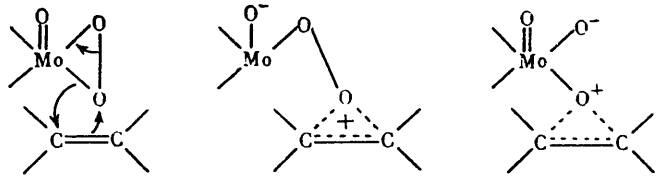
(XIX)

However, the reactions considered are significantly different in their nature. In contrast to molybdenum compounds, palladium compounds form complexes with olefins not only via donor–acceptor interactions but also via a dative interaction and are probably capable of adding to the double bonds. The formation of a C–Pd bond is indicated by the involvement in the reaction of only the terminal double bond, with a sterically accessible carbon atom, and also by the unusual hydride shift§. On the other hand, the formation of Mo–C and V–C

§ In the isomerisation of epoxy-compounds to aldehydes or ketones, the unoccupied orbital accepting the hydride anion arises at the more substituted carbon atom.[57]

bonds is unlikely, while the formation of five-membered complexes analogous to (XVIII) is inconsistent with experimental epoxidation data.[2,132] In particular, the comparable rates of epoxidation of cyclohexene and norbornene (an effective 1,3-dipolarophile)[132] are evidence against the 1,3-dipolar addition to the double bond.

The operation of ionic mechanisms in which compounds (XXI) and (XXII) are formed in organic (non-polar) media appears less probable than the synchronous mechanism involving the formation of compound (XX):



(XX) (XXI) (XXII)

The autoacceleration and inhibition effects, indicating that the competing associative process can promote or conversely hinder the insertion of the alkyl hydroperoxide and then the olefin in the coordination sphere of the catalyst, are characteristic of the alkyl hydroperoxide epoxidation[3] and of a series of heterolytic reactions of hydrogen peroxide and peracids.[55,56]

VII. STEREOSELECTIVITY AND REGIOSELECTIVITY OF THE HYDROPEROXIDE EPOXIDATION

Henbest and Wilson laid the foundations of stereoselective epoxidation having established that the allyl hydroxy-group in cyclohexenol is coordinated to the peracid and promotes *cis*-epoxidation.[133] The rate of reaction is then higher by an order of magnitude than in the case of the corresponding cyclohexenyl acetate.

Alkyl hydroperoxides showed an even greater selectivity in the oxidation of cyclic and saturated alcohols (see Table) in the presence of vanadium and molybdenum compounds.[126, 134-137] 2-Cyclohexanol was oxidised more readily than cyclohexene, while cyclohexene was more reactive when a peracid was employed.[134]

It is striking that the epoxidation of C_6–C_9 cycloalkenols with *m*-chloroperbenzoic acid (MCPBA) is accompanied by a change in the direction of attack by the reagents on passing from a seven-membered to an eight-membered ring (see Table). This finding can be accounted for by the conformational changes arising following an increase in ring size. On the other hand, under the conditions where a vanadium catalyst is used the coordination of the OH group to the central atom is so strong that it alters the conformation and ensures the *syn*-attack by the oxidant. A *syn*-directing influence is also shown by the hydroxy-group in 3-cyclohexenol.[134] In this case the molybdenum catalyst is more effective than the vanadium catalyst.

The most probable geometry of the transition state in the epoxidation of cyclohexenols by peracids and ROOH has been published by Itoh et al.[126] (see Section VI).

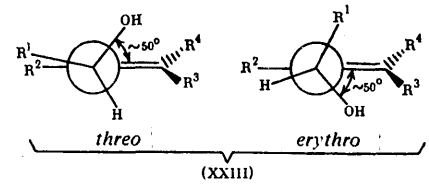
It is of interest to note the highly selective formation of *cis*-epoxyalcohols in the oxidation of cyclenes by atmospheric oxygen in the rpesence of vanadyl acetylacetonate[138] with the intermediate formation of allyl hydroperoxides. The catalytic reaction of the cycloalkenyl hydroperoxides themselves has been investigated[139] (see Table). The exclusive formation of *cis*-epoxyalcohols suggests that the epoxidation is intramolecular.

The directing influence of the hydroxy-group has been used successfully also in the hydroperoxide epoxidation of acyclic systems. A high regioselectivity (84–93%) has been attained in the catalytic epoxidation of geraniol, linalool,[134] and certain analogues of farnesol[140] by t-butyl hydroperoxide (see Table). ROOH epoxidises the allyl 2,3-double bond, while peracids oxidise preferentially the more remote 6,7-double bond.

The possibility of the selective hydroperoxide epoxidation of allyl alcohols of the type of (XXIII) (see Table) has been demonstrated.[136,141]

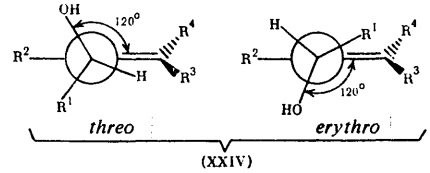
The Table shows that peracids exhibit a high stereoselectivity only for a specific structure of the alkenol (with $R^2 = H$). The presence of a single substituent at the C(3) atom in the *trans*-position lowers the stereoselectivity.[142]

The probable dihedral HO–C–C=C angles in the transition states leading to the *threo*- and *erythro*-isomers in oxidation of (XXIII) by ROOH and of (XXIV) by a peracid have been calculated:[140]



threo *erythro*

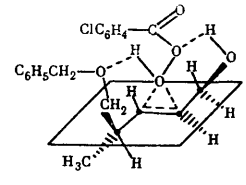
(XXIII)



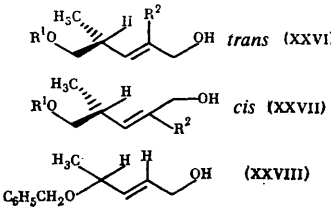
threo *erythro*

(XXIV)

An unusual effect of the joint directing effect of the hydroxy-group and the ester oxygen atom, as in (XXV), has been observed in the epoxidation of the olefinic alcohols (XXVI) and (XXVII), where $R^1 = C_6H_5CH_2$ or H and $R^2 = H$, CH_3 or $Si(CH_3)_3$, by MCPBA.[143,144] The stereoselectivity reaches 86–96%.



(XXV)



trans (XXVI)

cis (XXVII)

(XXVIII)

The high effectiveness of the joint influence of the substituents in the *cis*-isomer is determined, according to the authors,[144] by the geometry of the most stable conformation (XXVII). A similar effect of the functional groups in compound (XXVIII) was not observed.[145]

The directing influence of the bulky trialkysilyl group at the C(2) atom of the alkenol (see Table) is extremely effective.[144-146] In the final epoxyalcohol it can be readily substituted by hydrogen on treatment with $(n\text{-}C_4H_9)_4NF$ in DMF.

Evidently the discovery of the most stable conformation of the alkenol in the ground state and the selection of the corresponding substituents are extremely useful in carrying out the reaction with the expected stereochemical results, although the method,[147] based on the estimation of the relative stabilities of the diastereoisomeric transition compounds in accordance with the Curtin–Hammett principle, is more universal for the prediction of the mode of synthesis.

The stereoselectivity and regioselectivity of the epoxidation of certain substituted alkenes and cycloalkenes.

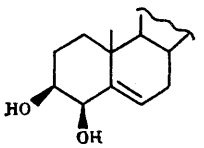
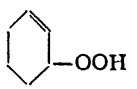
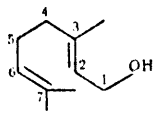
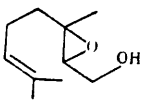
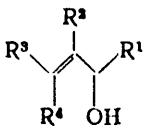
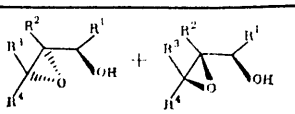
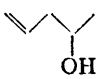
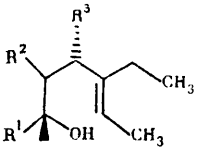
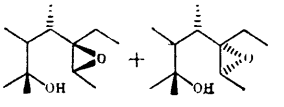
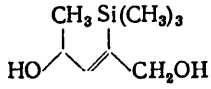
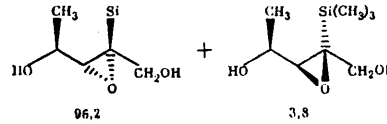
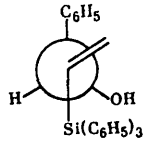
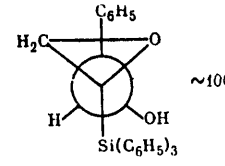
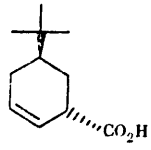
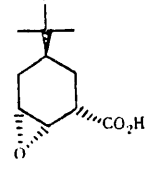
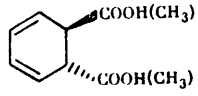
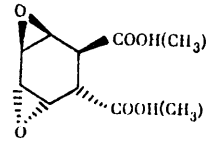
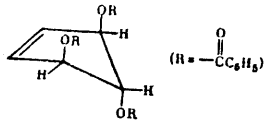
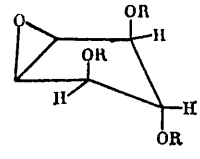
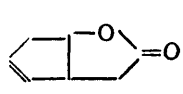
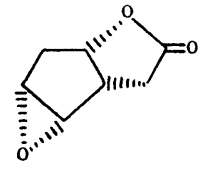
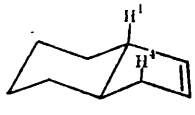
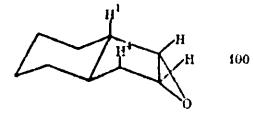
Olefin	Epoxidising agent, catalyst	Content of isomer, %	Refs.
Cyclic aliphatic 5-9-membered *Z*-allyl and 8-20-membered *E*-allyl alcohols, methylenecyclohexenols	t-C_4H_9OOH, $VO(acac)_2$ or $Mo(CO)_6$	*cis*-epoxyalcohols, 91-99	[126, 135, 136]
2-Cyclohexenol 2-Cycloheptenol 2-Cyclo-octenol 2-Cyclononenol	MCPBA ditto » »	*cis*-epoxyalcohol, 95 ditto », 61 » », 0.2 » », 0.2	[126, 133, 135]
3-Cyclohexenol	t-C_4H_9OOH, $Mo(CO)_6$	*cis*-epoxyalcohol, 90	[134]
 4β-Hydroxycholesterol	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	*cis*-epoxyalcohol, 100 *cis*-epoxyalcohol, 66	[134]
	$VO(acac)_2$	*cis*-epoxyalcohol, 100 (yield 79%)	[139]
 Geraniol	t-C_4H_9OOH, $VO(acac)_2$	 93	[134]
 R^2=H; R^3=R^4=H (XXIII)		 *R*R*(erythro)* *R*S*(threo)*	[136, 141]
	t-C_4H_9OOH, $VO(acac)_2$	14 86	
	t-C_4H_9OOH, $Mo(CO)_6$	5 95	
	MCPBA	5 95	
	t-C_4H_9OOH, $VO(acac)_2$	95 5	
	t-C_4H_9OOH, $Mo(CO)_6$	84 16	
	MCPBA	55 45	
	p-NO_2PBA	68 32	
 Pent-4-en-2-ol	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	66 34 55 45	[148, 149]
 Ditto	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	 85-95 15-5 non-stereoselectively	[150]

Table (contd.)

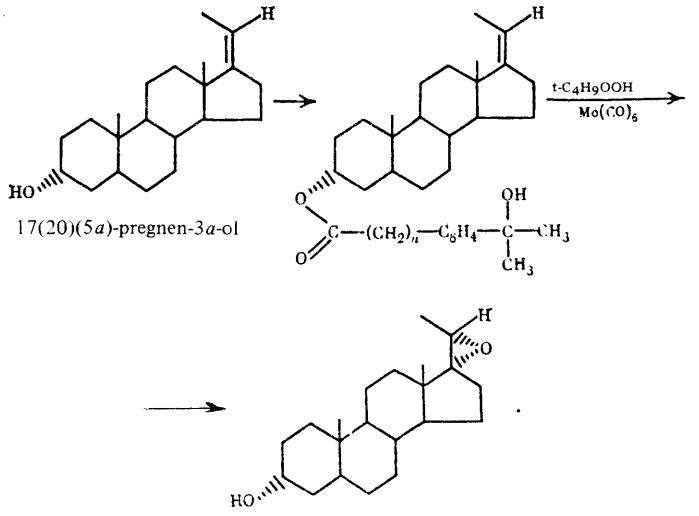
Olefin	Epoxidising agent, catalyst	Content of isomer, %	Refs.
	MCPBA	 96,2 3,8	[145]
	MCPBA	 ~100	[146]
	MCPBA, or CH_3CO_3H, or polymeric peracids in inert solvents	 77-79	[154]
	MCPBA	 ~100	[155]
	CF_3CO_3H	 ~100	[159]
 Ditto » »	CH_3CO_3H in HAc MCPBA in hexane MCPBA in CCl_4	 89 Ditto, 80 Ditto, 40	[160]
	*p*-NO_2PBA	 100	[161]

Estimation of the strain induced by the interaction of the substituents in the 1-, 2-, and 3-positions in the allyl alcohol makes it possible to predict the structure of the optimum transition state and the result of the reaction as a whole, which has been demonstrated for a series of examples described in the literature.

The stereochemical course of the epoxidation reactions of acyclic 3- and 4-alkenols has been investigated only for individual examples (see Table). Thus pent-4-en-2-ol exhibits only a weak 1,3-asymmetric induction in its reactions with various oxidants,[148,149] while 4-alkenols are epoxidised by t-C_4H_9OOH with a high stereoselectivity (1,4-asymmetric induction).[150]

The stereospecific epoxidation of the olefin bond in steroids[151] and acyclic polyenes[152] has been carried out making use of the influence of a very remote OH group. For this purpose, it was acylated by a hydroxylated reagent (template). The size and geometry of the template enabled

the OH group present in it to cooperate with the oxidant:

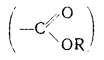


17(20)(5*a*)-pregnen-3*a*-ol

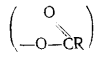
The asymmetric epoxidation of allyl alcohols by alkyl hydroperoxides has been carried out in the presence of vanadium and molybdenum complexes incorporating chiral ligands: hydroxamic acids[127] and *N*-alkylephedrin.[153] The asymmetric induction reached 50%.

The influence of other functional groups on the stereoselectivity of the epoxidation has also been investigated (see Table). The epoxidation of certain βγ-unsaturated acids of the cyclohexene series by peracids has been studied.[154] The tendency towards *cis*-epoxidation relative to the carboxy-group (54–79%) has been observed in inert solvents. The methyl esters of the above acids are epoxidised independently of the medium with the preferential formation of the *trans*-isomers (60–64%). The oxidation of *trans*-1,2-dihydrophthalic acid by MCPBA leads exclusively to mono- and di-epoxides with the *cis*-disposition of neighbouring epoxy- and carboxy-groups even in a weakly basic solvent—ethyl acetate.[155]

The presence of the carboxylate



or acyloxy-group

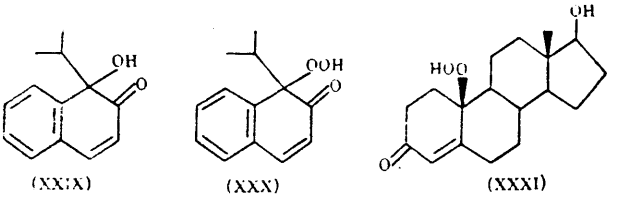


in the ring usually leads to the *trans*-orientation of the oxidant.[133,154,156,157] Nevertheless, when such substituents accumulate, for example, in the case of dimethyl *trans*-1,2-dihydrophthalate[158] or the tribenzoate of cyclopentenetriol,[159] a specific *syn*-directing influence is manifested (see Table).

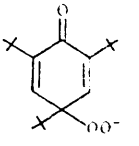
It has been established that the stereochemistry of the epoxidation of the lactone of 2-hydroxy-4-pentenylacetic acid by peracetic acid depends significantly on the nature of the solvent, indicating a relation between the conformation of the molecule and the conditions governing the solvation of the functional group.[160] The mode of epoxidation of unsaturated rings of moderate size does not exhibit a definite dependence on the orientation of the epoxy-group present in them.[161–163]

Dynamic conformational analysis of the epoxidation of substituted five-, six- and seven-membered cyclic olefins and certain bicyclenes[164] showed that the direction of attack by the reagent involving the least conformational distortions predominates. The principles developed in the last study quoted can be used in the planning of a stereospecific synthesis.

The stereoselective synthesis of epoxides from chalcones and naphthoquinones has been carried out with the aid of alkaline hydrogen peroxide or ROOH.[165–168] The use of chiral quaternary ammonium salts based on quinine and quinidine as phase-transfer catalysts made it possible to achieve an excess of one of the enatiomers to the extent of 25–55%. The epoxidation of 1-hydroxy-1-isopropylnaphthalen-2(1*H*)-one (XXIX) with alkaline hydrogen peroxide[169] takes place exclusively in the *trans*-position relative to the hydroxy-group. On the other hand, the intramolecular oxidation of the multiple bond in compounds (XXX),[170] (XXXI),[171] and (XXXII)[172] leads to *cis*-epoxyalcohols:



(XXIX) (XXX) (XXXI)

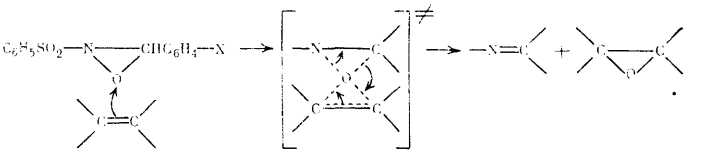


(XXXII)

A rigorously selective intramolecular epoxidation of the multiple 14,15-bond occurred in peracids derived from polyenoic acids: eicosa-*cis*-5,8,11,14-tetraenoic and eicosa-*cis*-8,11,14-trienoic acids.[173] The intramolecular oxidation of hydroperoxides obtained from certain orthoesters and ketals[113] by the method described in Ref. 112 takes place with the olefin double bond much less remote from the peroxide oxygen.

VIII. OXAZIRIDINES AND HETEROCYCLIC EPOXIDISING INTERMEDIATES

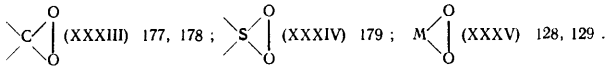
Oxaziridines containing electron-accepting substituents are capable of oxidising sulphides, amines, organometallic compounds, and olefins:[174]



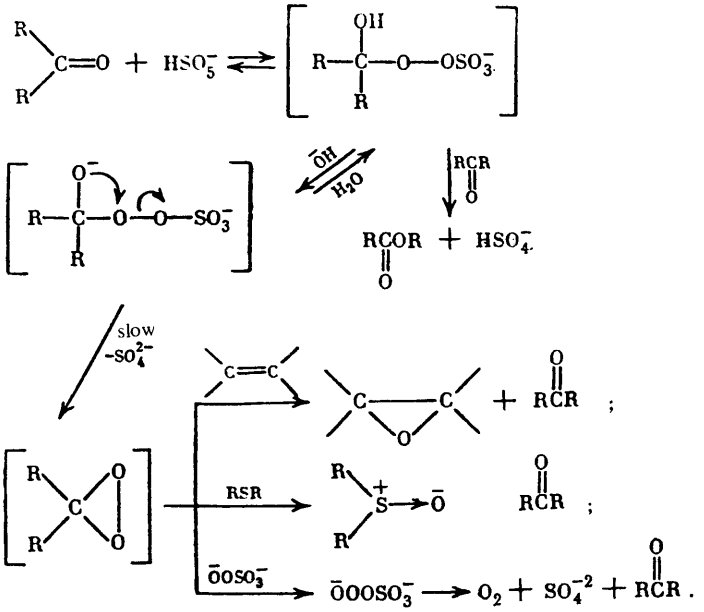
For example, *trans*-stilbene is epoxidised by 2-arenesulponyl-3-aryloxaziridines at 60 °C in the course of 10–12 h with a 95% yield of the epoxide¶.

¶ For comparison, one may note that under severe conditions oxirans are capable of transferring oxygen to phosphines (150 °C),[175] while sulphur dioxide can transfer oxygen to ethylene (400 °C).[176]

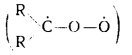
In certain reactions involving peroxy-compounds, ozone, or singlet oxygen, the formation of highly reactive intermediates (XXIII) and (XXIV), resembling an oxaziridine, has been postulated:



The peroxy-compounds of certain transition metals (XXXV) have been isolated and investigated as epoxidising agents. The formation of the dioxiran (XXIII) has been suggested in the decomposition of potassium peroxymonosulphate (potassium Caroate—$KHSO_5$) in the presence of a ketone: [177]



In water at pH 7.5 and a temperature of 2–10 °C the dioxiran epoxidises, also in the absence of a ketone, αβ-unsaturated ketones, acids, and their esters (which cannot be oxidised either by peracids or potassium Caroate) as well as the usual olefins. The Baeyer–Villiger reaction takes place at a negligible rate under these conditions. The reaction is rigorously stereospecific, which rules out the involvement of the carbonyl oxide

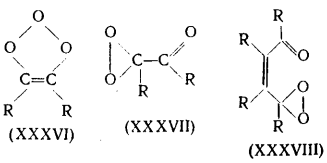


in it.

As a very powerful oxidant, the dioxiran can transfer active oxygen to the peracid anion with the subsequent formation of singlet oxygen. The rate of decomposition of the peroxymonosulphate anion is described by the equation [180]

$$W = k\cdot[HSO_5^-]\,[\text{ketone}]\,[\bar{O}H].$$

It has been suggested that the ozonisation of alkynes [178,181] results in the formation, together with peracids, of the epoxidising intermediates (XXXVI) and (XXXVII), the dioxiran (XXXVII) oxidising alkenes non-stereospecifically:

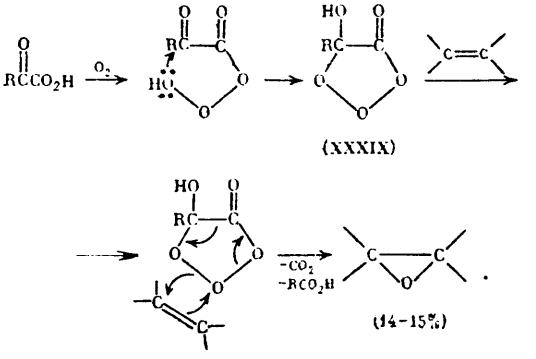


Compounds (XXXVI) and (XXXVII) are extremely reactive and epoxidise olefins at −70° and −25 °C respectively.

The dioxiran (XXXVIII) is regarded as an intermediate which transfers oxygen in the epoxidation of tetramethylethylene to the endoperoxides of furan and its derivatives. [182]

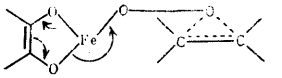
The sulphur-containing analogue of dioxiran (XXXIV) or its isomer sulphenyl oxide ($S=\dot{O}-\bar{O}$) is formed, according to Martin and Martin, [179] under the conditions of the oxidation of a compound of tetracovalent sulphur by hydrogen peroxide in the presence of cyclohexene or norbornene at −78 °C. An increase of temperature to room temperature completes the epoxidation reaction.

The oxidative decarboxylation of α-ketoacids with the aid of singlet oxygen, which proceeds via the trioxolan (XXXIX) capable of transferring oxygen to olefins, including tetracyanoethylene, in the temperature range from −100° to −150 °C, has been described: [183]

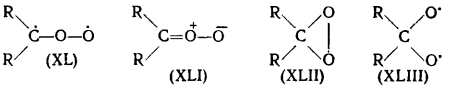


IX. THE OXENOID MECHANISM. CARBONYL OXIDE AND ITS ANALOGUES

By analogy with carbenoid, the term oxenoid is applied to the kinetically unstable species capable of transferring oxygen with a sextet of electrons to the substrate and of being converted into a neutral molecule. In his study of the enzymic oxidation of olefins by molecular oxygen, [184] Hamilton proposed the "enediol–Fe–O_2" oxenoid model, which transfers oxygen to the substrate:



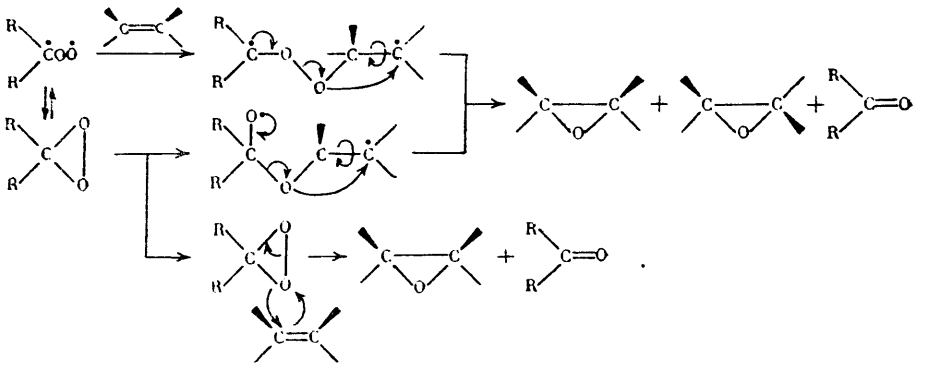
However, it has been suggested [185] that the consumption of peroxide in such systems proceeds via a radical chain mechanism. The "carbonyl oxide" (XL) or (XLI) (the Criegee intermediate) is a typical oxenoid. The dioxiran (XLII) and "methylene dioxide" (XLIII) are isomers of compound (XL): [178, 186–188]



Quantum-chemical calculation has shown that, as regards energy, the dioxiran is more favourable by 33.7–36 kcal than carbonyl oxide and by 15 kcal than methylene dioxide. [189,190]

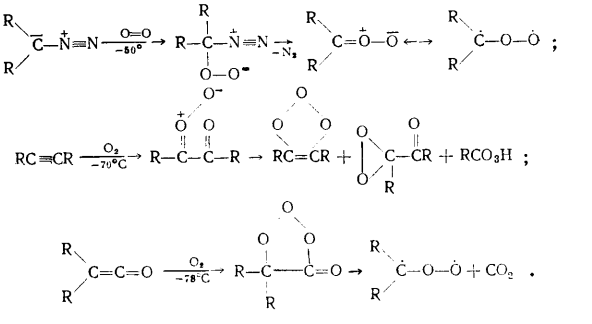
The oxenoid mechanism presupposes the involvement of any of the species indicated in the epoxidation reaction. One cannot rule out the possibility that the olefin can induce the homolytic rupture of the bonds in compound (XLII), abolishing the results of the interaction of olefins with compound (XL), (XLII), and (XLIII).

The epoxidation of olefins by carbonyl oxide and its isomers allows the formation of a biradical intermediate and rotation about the σ-bond: [186,187,191]



This mechanism is supported by the partial stereospecificity of the reaction. For example, *trans*-hex-3-ene gives rise to 99% of the *trans*-epoxide and 1% of the *cis*-isomer, while *cis*-hex-3-ene produces 95% of the *cis*-epoxide and 5% of the *trans*-isomer.

Carbonyl oxide is formed when diazomethane is treated with singlet oxygen[186] and when acetylenes,[178] ketenes,[187,188] and olefins[191] are ozonised:



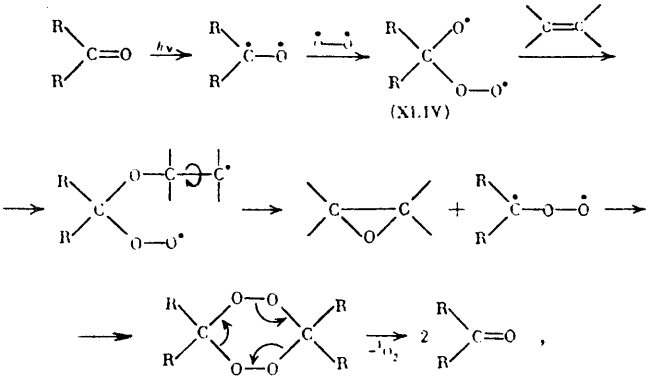
The ozonisation of olefins is known to lead to the formation of ozonides—the products of the coupling of Criegee intermediates with a carbonyl compound. However, in the presence of tetracyanoethylene, which is an effective 1,3-dipolarophile and which is not ozonised at a low temperature (−78 °C), epoxytetracyanoethane is formed in a quantitative yield.[192] Tetramethylethylene and norbornene are not epoxidised under these conditions.

It follows from the study of Gillies[191] that other electron-deficient olefins, namely symmetrically fluorinated ethylenes, can be epoxidised by carbonyl oxides. Ozonolysis of perfluoro- and 1,2-difluoro-ethylenes differs from that of the geminal difluoro-olefins and the usual alkenes. The study of the deuteriated substrates showed that the reaction takes place with partial cleavage of the olefin and with attack by fluorocarbonyl oxide on the olefin.

Evidently the introduction of an electron-accepting substituent into carbonyl oxide weakens its nucleophilic properties and its ability to attack the carbonyl group, permitting an electrophilic attack on the olefin.

By analogy with the dioxiran (XXXVII), the trioxides (XXXVI) and (XXXIX) and the sulphenyl oxide (XXXIV), mentioned above, may be included among oxenoid oxygen transferring agents.

The biradical (XLIV), formed as an intermediate in the photochemical oxidation of many cyclic and acyclic olefins sensitised by aliphate α-diketones or benzophenone, is also regarded as a probable epoxidising agent:[193]

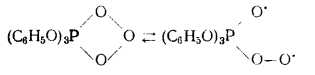


(XLIV)

Regardless of the geometry of the initial olefin, only the *trans*-epoxide is formed in the reaction. Benzophenone is then hardly consumed and, despite a fivefold excess of the olefin, a high yield of the oxiran is ensured.

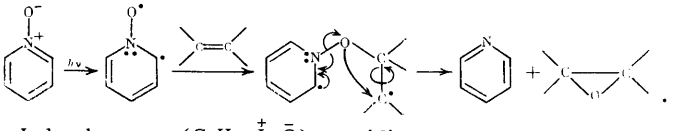
One should note that certain related photochemical epoxidation reactions in the presence of benzoin[194] and α-ketoacids[195] have been explained by the epoxidising action of acylperoxy-radicals. In this case the sensitisers are consumed as reactants.

The analogue (XLIV), which is a triphenylphosphite ozonoid,



exhibits a weak epoxidising activity.[186]

The *N*-oxides of nitrogen-containing heterocycles,[196,197] idosobenzene,[198] and phenylbenozyldiazomethane (azibenzil) are oxenoid reagents in the presence of oxygen.[199] Oxygen transfer to olefins by the *N*-oxide takes place under the conditions of photolysis at −70 °C and is characterised by the absence of stereo specificity: a *cis*-olefin gives rise to a 1:1 mixture of the *cis*- and *trans*-epoxides. Preliminary isomerisation of the *N*-oxides to oxaziridines is ruled out, because the latter epoxidise olefins stereospecifically.[176] The epoxidation mechanism can be accounted for if the *N*-oxide fragment $-C=\overset{+}{N}-\bar{O}$ is regarded as a heteroanalogue of carbonyl oxide:



Iodosobenzene ($C_6H_5-\overset{+}{I}-\bar{O}$) epoxidises and hydroxylates hydrocarbons in the presence of catalysts: iron αβγδ-tetraphenylporphyrinate and chlorodimethylferriprotoporphyrin. The system is very sensitive to the structure of the olefin

and the catalyst ligands. It has been suggested that iodosobenzene transfers oxygen to the substrate via a "catalyst–oxygen" intermediate.

A complex epoxidising olefins is formed from azilbenzil $C_6H_5COC(N_2)C_6H_5$ on interaction with oxygen in the presence of palladium acetate. The reaction with *cis*-olefins loses its stereoepcificity. It is believed[199] that the catalyst accelerates the decomposition of azibenzil and promotes the formation of a ketocarbene–oxygen complex, which plays the role of oxenoid.

The action of an alkaline solution of xenon trioxide and sodium perxenate (Na_4XeO_6) on an olefin has been investigated.[200,201] In contrast to certain inorganic oxides (OsO_4, MnO_4^-), which induce *cis*-1,2-hydroxylation, XeO_3 produces only epoxides, like peroxide reagents.

The ratio of the rates of epoxidation of norbornene and cyclohexene is small (2.4–2.7) and is evidence against a five-membered transition state characteristic of 1,3-dipolar addition.

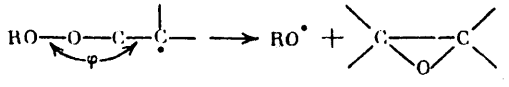
At the same time the weak stereospecificity of the reaction rules out the possibility of the operation of a typical synchronous mechanism with a three-membered transition state. The reaction apparently proceeds via the oxenoid mechanism involving the formation of a weakly bound bridged three-membered complex, permitting homolytic ring opening and rotation about the σ-bond.

X. SOME ASPECTS OF RADICAL EPOXIDATION

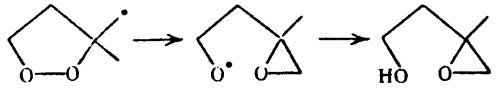
The epoxidation of olefins by alkyl- and acyl-peroxy-radicals has been described in a review.[122] Reaction of this type are non-stereospecific, which indicates a multistage mechanism of the formation of the ring. According to Sawaki and Ogata,[194] the *trans*-selectivity of the epoxidation by acylperoxy-radicals follows from the relative stabilities of the two possible transition states in the epoxide ring closure stage—the state with the transoid disposition of the bulkiest substituents is preferable.

The radical adduct $(CH_3)_2N{-}O{-}O^{\cdot}$, formed in the epoxidation of many olefins by oxygen in the presence of amines and a Lewis acid ($ZnCl_2$), has been considered as an analogue of an acyl peroxy-radical.[202] Under the influence of the amine, the oxirans are converted into aminoalcohols under the conditions of the synthesis, although in the case of cyclooctene the intermediate oxiran was isolated.

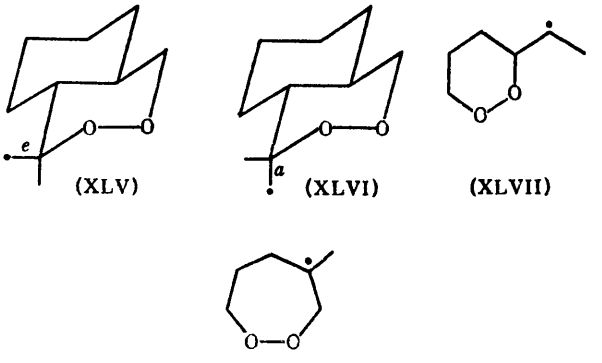
Important data about the stereochemistry of the epoxide ring closure in peroxyalkyl radicals have been published.[203,204] It has been shown that an angle close to 180° between the bonds of the leaving alkoxy-radical and the attacking carbon atom carrying the unpaired electron is a condition for the homolytic substitution at the peroxide oxygen atom (S_H):



Thus the formation of epoxyalcohols in accordance with the scheme



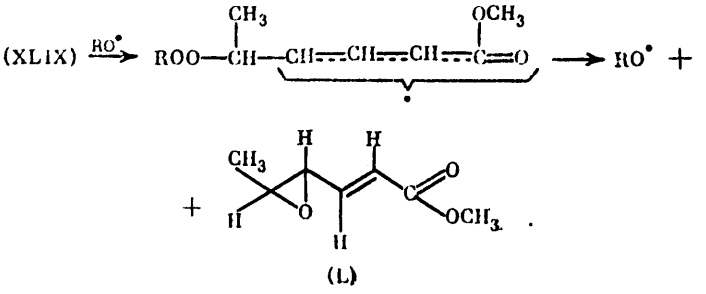
has been observed only in the radicals (XLV) and (XLVII) and not in their analogues (XLVI) and (XLVIII):



(XLV) (XLVI) (XLVII)

(XLVIII)

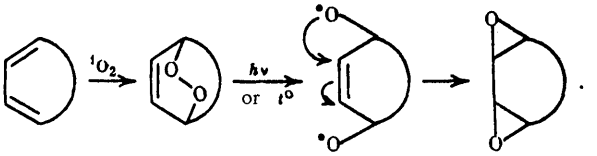
In contrast to the typical non-stereospecific epoxidation of olefins by alkyl- and acyl-peroxy-radicals, conjugated dienones and diene esters are epoxidised by molecular oxygen strictly stereo- and regio-selectively at the γδ-double bond.[205] For example, methyl sorbate (XLIX) forms exclusively the *E*, *E*-epoxide (L):



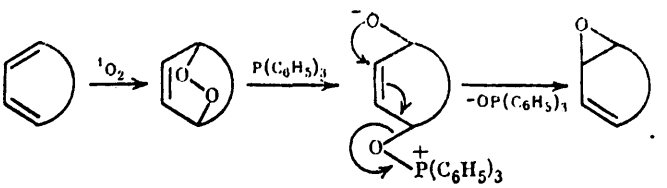
(L)

The stereospecific free-radical epoxidation of 7,8-dihydroxy-7,8-dihydrobenzo[*a*]pyrene by the hydroperoxides of polyunsaturated aliphatic acids has been noted.[206]

In the synthesis of bisepoxides from cyclic 1,3-dienes, the method used involved the oxygenation of the latter compounds by singlet oxygen with subsequent photochemical or thermal isomerisation of the resulting *endo*-peroxides:[207]



This entails the exclusive formation of *cis*-diepoxides. The deoxygenation of the *endo*-peroxide by triphenylphosphine leads to monoepoxides:

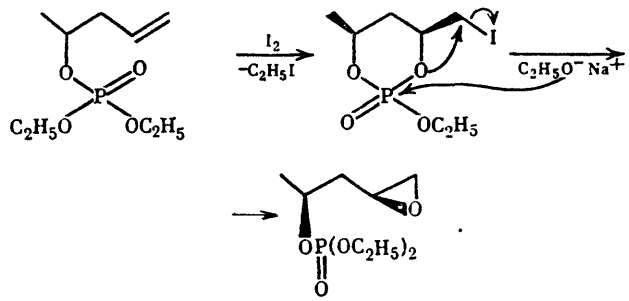


Combination of the above methods with the methods for the oxidation of olefins with the aid of peracids and via halogenohydrins gives rise to the possibility of the specific synthesis of di-, tri-, and poly-epoxides from hepta and octa-trienes

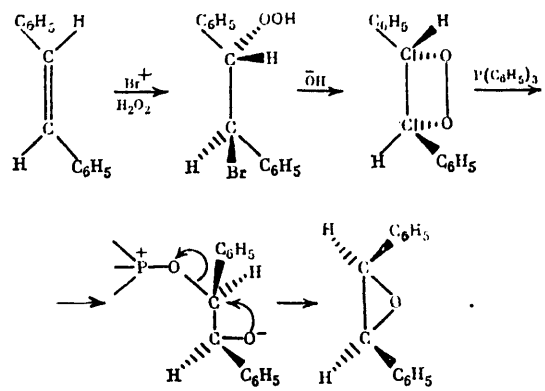
as well as other cyclic polyenes.[162,163,208] The strained system of the cyclopentadiene *endo*-peroxide gives rise to many side products on thermolysis (epoxyketones, ketoalcohols, and others).[209] On the other hand, in the case of substituted cyclopentadienes the yield of diepoxides is much higher.

XI. THE SYNTHESIS OF OXIRANS BASED ON INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION

A number of methods for the stereospecific synthesis of oxirans have been proposed. Bartlett and Jernstedt[148] achieved a highly stereoselective epoxidation of 3-alkenols by the iodination of the corresponding phosphates:[148]

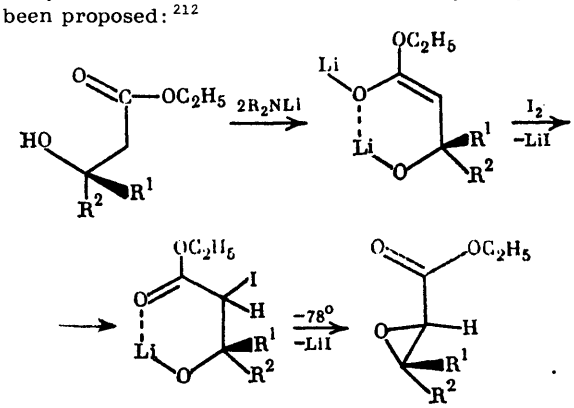


A stereoselective conversion of *trans*-stilbene into the *cis*-epoxide with a threefold inversion of the substrate[209] has been achieved via the deoxygenation of dioxetan with triphenylphosphine:



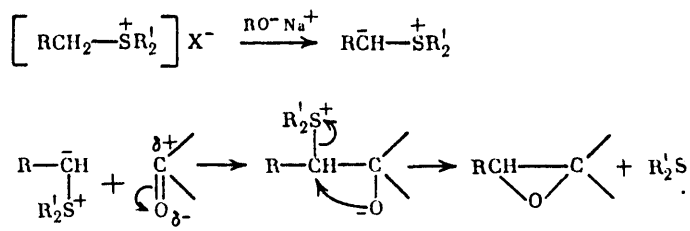
The deoxygenation of cyclo-1,3-diene *endo*-peroxides takes place similarly in the presence of triphenylphosphine.[207] The halogenoactonisation procedure has been used for the epoxidation of unsaturated acids[210] and alcohols:[211]

A new method for the stereoselective synthesis of αβ-epoxyesters by the oxidation of the dianions of β-hydroxyesters has been proposed:[212]



The high degree of asymmetric induction in such syntheses is due to the conformational features of the intermediate cyclic complexes, which make one of the pathways to the electrophilic addition to the double bond preferable.

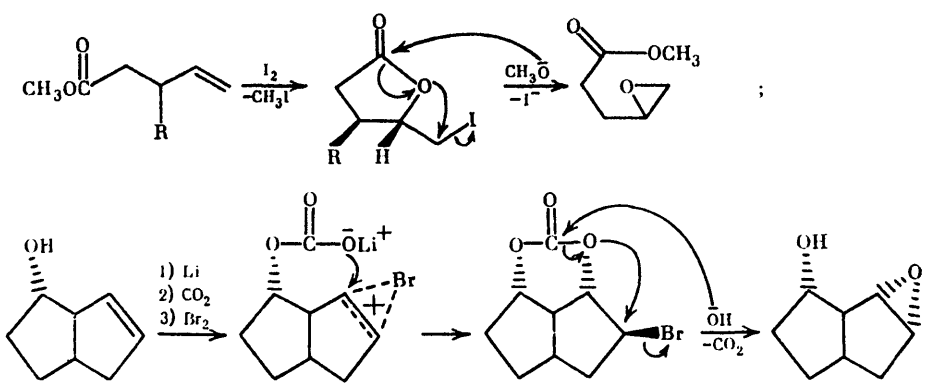
The method of synthesis of oxirans based on the coupling of sulphonium ylides to oxo-compounds has been described in several reports:[213–215]

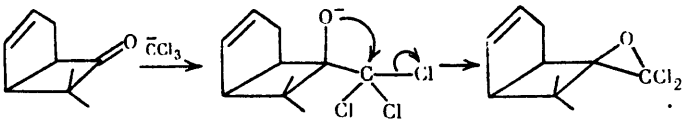


An alkyl phenyl sulphide can be the leaving group in an alkaline medium in the presence of a hydroxy-group in the α-position,[91] which has been used in the synthesis of an optically active epoxide–disparlure.

A series of new syntheses, in which the epoxide ring is closed by the Darzens method have been described, for example, the epoxyannelation of the carbanions of β-ketoesters and β-diketones to 1,4-dichlorobutan-2-one[216] and the condensation of α-mercaptocarbonyl compounds with 2-chloroacrylonitrile in the presence of tetraalkylammonium iodide as the catalyst.[217]

Under the conditions where a phase-transfer catalyst is used, dichloroepoxides, which readily rearrange to the chlorides of carboxylic chloroacids, have been obtained from ketones and chloroform in an alkaline medium:[218]





The epoxidation of styrene and cyclohexene by sodium hypochlorite, catalysed by transition metal complexes in the presence of a phase-transfer catalyst, has been described.[219]

Oxirans can be obtained from vicinal diols by treating the latter with an equimolecular amount of tosyl chloride and powdered sodium hydroxide.[220] The epoxide ring is reduced after the tosylation of one hydroxy-group.

The C_2–C_{18} alkane-1,2-diols are dehydrated with formation of epoxides also in the gas or liquid phase at 250–550 °C in the presence of basic catalysts (AcONa, $Na_2B_4O_7$, Na_3PO_4, etc.).[221] The thermolysis of chlorohydrin esters at 150–250 °C in the presence of catalysts (ammonium of phosphonium salts) leads to the same result.[222]

The survey of the literature data makes it possible to differentiate five types of mechanisms of the epoxidation of olefins.

The first type includes many-centre synchronous mechanisms of the transfer of oxygen by the peroxide reagent to the substrate, which are completely stereospecific.[56,125,126,143] The synchronous mechanism is characteristic of many instances of hydroperoxide oxidation in the presence of protic or aprotic acids and bases whose composition constantly varies during the reaction. The competing associated processes taking place in such systems, in particular the non-equilibrium solvation of the reactants, exert a major influence on the rate and direction of the chemical reactions, producing a number of kinetic effects: autocatalysis, inhibition, dependence of the specific rate (k) and the activation parameters on the concentrations of the reactants and acid–base associated species, etc.

The second type involves an ionic mechanism which operates in the epoxidation of polar olefin bonds by hydrogen peroxide or alkyl hydroperoxides in an alkaline medium.[56,83,166] In the aliphatic series, *trans*-selectivity due to the rotation about the C–C bond in the intermediate carbanion, is observed.

The next type involves a radical asynchronous mechanism, presupposing the formation of a monoradical[122] or biradical[186,193,196] intermediate complex whose life span is sufficient for the inversion of the configuration of the initial olefin. A conformational equilibrium, mainly in favour of the *trans*-isomer of the oxiran, is then established, which renders the reaction non-stereospecific. An exceptional case of *cis*-selectivity has been described.[223]

Stereospecific radical epoxidation also occurs.[122,205]

Reactions whose mechanism is based on the nucleophilic closure of the epoxide ring constitute a separate group. The following are the usual leaving groups: Hal,[148,211,218] SR_2,[213,214] and OH.[220,221] The electrochemical epoxidation can be included in the same type.[224,225]

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