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The Mechanism and Stereochemistry of the Oxidation of Bicyclic Hydrocarbons with a Bridge Bond

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Reactions involving the oxidation of unsaturated bicyclic hydrocarbons with a bridge bond by oxygen, hydroperoxides, peracids, and hydrogen peroxide are examined, particular attention being devoted to the mechanism and the stereochemistry of the oxidation of norbornene hydrocarbons and their derivatives.
The bibliography includes 98 references.

CONTENTS

I.	Introduction	915
II.	Autoxidation	915
III.	Interaction with hydroperoxides	918
IV.	Oxidation by peracids	920
V.	Reactions with hydrogen peroxide	921

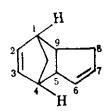
I. INTRODUCTION

Bicyclic hydrocarbons with a bridge bond include a series of important natural compounds (terpenes). Since the beginning of the 1960s, individual representatives of hydrocarbons of this class (bicyclic olefins—mainly norbornene and its homologues) have been finding increasing practical applications as monomers[1-4] for the manufacture of high-molecular-weight compounds with valuable technical properties, obtained mainly by solution polymerisation and copolymerisation in the presence of Ziegler–Natta catalysts.

Owing to their complex steric structure, bicyclic hydrocarbons with a bridge bond are excellent objects for the study of the mechanisms and stereochemical characteristics of chemical reactions[5-7], among which the oxidation reactions are of special interest.

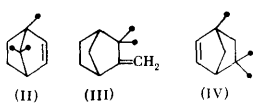
II. AUTOXIDATION

Having autoxidised dicyclopentadiene (I), Hock and Depke[8] found that the primary reaction products are derivatives with hydroperoxy-groups in the 5- and 8-positions; the 1- and 4-positions (at the bridgehead of the bicyclic system) remain unaffected.



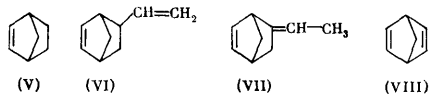
(I)

The oxidation of certain bicyclic hydrocarbons—derivatives of bicyclo[2,2,1]heptane—was described most fully for the first time by Nesmeyanov et al.,[9] who showed that bornylene (II), camphene (III), and δ-fenchene (IV), i.e.



(II) (III) (IV)

are hardly oxidised by oxygen in the presence of cobalt and manganese stearates. Similar results were also obtained when an attempt was made to oxidise norbornene (V), vinylnorbornene (VI), ethylidenenorbornene (VII), and norbornadiene (VIII)[10,11] (Fig. 1).



(V) (VI) (VII) (VIII)

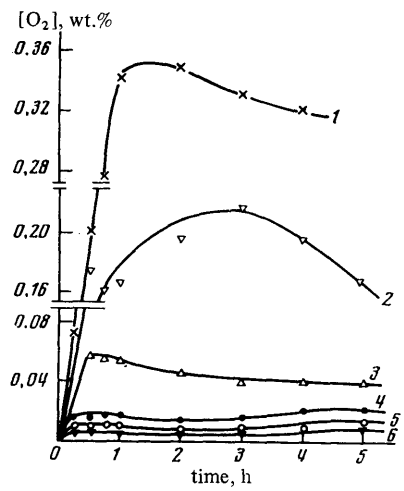


Figure 1. Kinetic curves for the accumulation of hydroperoxides (calculated in relation to active oxygen) at 95°C: 1) vinylcyclohexene; 2) tetrahydroindene; 3) dicyclopentadiene; 4) vinylnorbornene; 5) ethylnorbornene; 6) norbornene.

Nesmeyanov[9,12] explained the chemical passivity of the α-C_{tert}–H bond in the above systems as follows: the reactivity of the C–H bond in hydrocarbons depends on its strength, which diminishes in the presence of σ,π-conjugation. The latter takes place to the maximum extent only when the C–H bond and the axes of the "π-electron" clouds

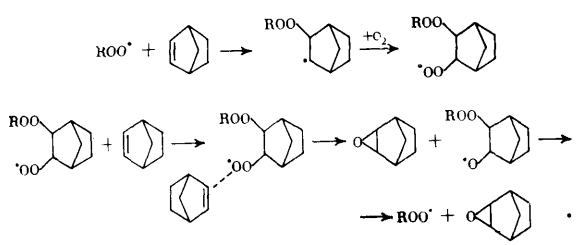
are nearly parallel; on the other hand, if they are at right angles, there is no conjugation and it has no influence on the C–H bond. In the above hydrocarbons (I)–(VIII), the α-C$_{tert}$–H bond is firmly fixed nearly at right angles to the axes of the "π-electron" clouds, which removes the α-C$_{tert}$–H bond from the σ,π-conjugation and reduces its chemical reactivity. It follows from Nesmeyanov's ideas that the axial α-C–H bond should show the greatest tendency towards oxidation in cyclic olefins, because, in contrast to the equatorial C–H bond, it exhibits the maximum degree of σ,π-conjugation, which has been confirmed experimentally[11,13].

A subsequent explanation of the passivity of the α-C$_{tert}$–H bond in bicyclo[2,2,1]heptane derivatives is associated with hypotheses concerning the structure of the transition state[14]. The hydroperoxide—the primary oxidation product—is known[15] to be formed via the mechanism

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}.$$

The formation of the radical R$^{\cdot}$ involves the transition of the carbon atom in the C–H bond from the sp^3-hybrid state to the sp^2-hybrid state. Since the rigid structure of bicyclo[2,2,1]heptane derivatives preclude such transition, then evidently the C–H bonds in this hydrocarbon must be chemically passive in radical reactions, in agreement with experiment[10]. It is noteworthy that the idea of taking into account the ring energy in considering the structure of the transition state has been used to explain the different rates of oxidation of C_5–C_{10} cycloparaffins[16].

Data on the oxidation of bicyclo[2,2,1]hept-2-ene in the presence of initiators proved to be extremely interesting. Mayo[17] observed that, when bicyclo[2,2,1]hept-2-ene is oxidised by oxygen in the presence of azobisisobutyronitrile (AIBN), an epoxy-derivative is formed. It was shown subsequently[18] that the epoxide is the main product of the oxidation of bicyclo[2,2,1]hept-2-ene derivatives by oxygen in the presence of not only AIBN but also of benzoyl peroxide. The study of the mechanism of the oxidation of bicyclo[2,2,1]hept-2-ene derivatives[10,19] showed that the formation of the epoxide from norbornene is described by the following mechanism:



The mechanism agrees satisfactorily with the reaction kinetics.

The main cause of this type of oxidation of norbornene and its derivatives is the presence of a strained double bond in their ring systems. A strained double bond is understood as one involving appreciable angular distortions and therefore possessing a large potential energy. The strain of the double bond is estimated experimentally from heats of hydrogenation[20,21] (as a rule a large absolute negative heat of hydrogenation corresponds to a large strain of the double bond in the system):



Hydrocarbon					
$-\Delta H_{hydr}$, kcal mole^{-1}	28,9	33.1	35,0	35,0	37.6

Comparison of the rates of initiated oxidation of cyclohexene and norbornene (Fig. 2) and also of the reaction products led to the hypothesis that the double bond of norbornene undergoes homolysis to a greater extent than that of cyclohexene[11], possibly because the p_z orbitals of the norbornene double bond overlap to a lesser extent than the p_z orbitals of the double bond of cyclohexene. This view has been confirmed by a comparison of the relative rates of autoxidation of hydrocarbons of different classes[22] (Table 1). Table 1 shows that olefins are oxidised much more readily than aromatic alkylhydrocarbons. The explanation is probably that the degree of conjugation in the allyl group is greater than in the benzyl group. The products of the oxidation of olefins (as well as cyclo-olefins) are hydroperoxides, unsaturated alcohols, and ketones, i.e. the products of oxidation involving C–H bonds in the α-position relative to the double bond. High rates of autoxidation are also characteristic of norbornene hydrocarbons, but here the ring double bond is oxidised and not the α-C–H bond.

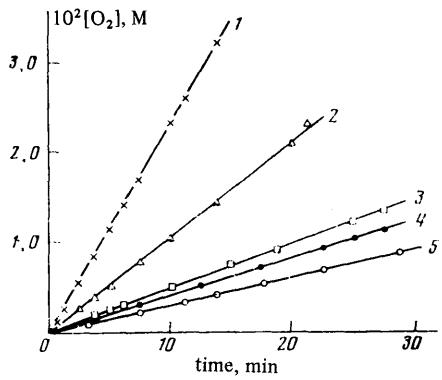
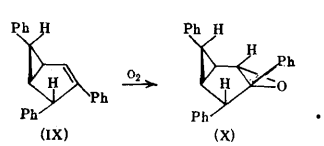


Figure 2. Kinetic curves for the absorption of oxygen at 50°C in the presence of AIBN (0.0304 M): 1) tetrahydroindene; 2) ethylidenenorbornene; 3) cyclohexene; 4) vinylnorbornene; 5) norbornene.

Table 1. The relative rates of autoxidation of hydrocarbons[22].

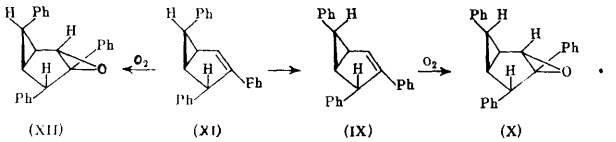
Hydrocarbon	k_{rel}	Hydrocarbon	k_{rel}	Hydrocarbon	k_{rel}
Cyclohexene	10.15	2-Methylbut-1-ene	6.54	Isopropylbenzene	1.00
Cyclopentene	9.34	Indan	4.30	Ethylbenzene	0.83
2-Methylbut-2-ene	8.50	*p*-Ethyltoluene	1.30	*p*-Xylene	0.73
Dicyclopentadiene	8.21	*p*-Isopropyltoluene	1.27	*m*-Xylene	0.67
Norbornene	7.82	*o*-Ethyltoluene	1.05	Toluene	0.28

A study of the oxidation of the stereoisomers of 3,4,6-triphenylbicyclo[3,1,0]hex-2-ene in xylene[23] showed that the *exo*, *exo*-isomer (IX) gives rise to the *exo*,*exo*-epoxide (X):



(IX) (X)

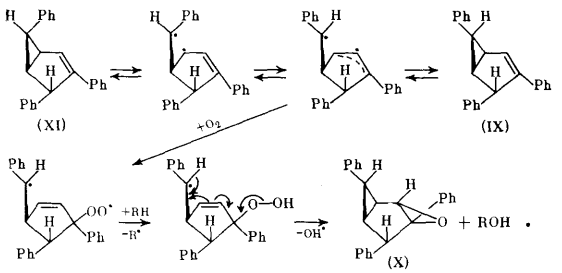
On the other hand, the oxidation of *exo,endo*-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene (**XI**) results in the formation of *exo,exo*-2,4,6-triphenylbicyclo[3,1,0]hex-2-ene (**IX**) and its *exo,exo*-epoxide (**X**) together with the corresponding *exo,endo*-epoxide (**XII**):



(XII) (XI) (IX) (X)

Evidently, in this case hydrocarbon (**XI**) is not only converted into the epoxide (**XII**) but also isomerises to hydrocarbon (**IX**), which is oxidised to compound (**X**). To demonstrate the occurrence of the isomerisation process, the authors[23] heated hydrocarbon (**IX**) or (**XI**) in nitrogen and obtained an equilibrium mixture of hydrocarbons (**IX**) and (**XI**) in proportions of 16 : 1.

A mechanism for the formation of products (**IX**) and (**X**) from compound (**XI**), according to which the rupture of the cyclopropane ring of the bicyclo-olefin leads to an intermediate biradical which then interacts with oxygen to form a peroxy-radical, was proposed on the basis of literature data[24,25]. The subsequent reactions of the peroxy-radical lead to products (**IX**) and (**X**):

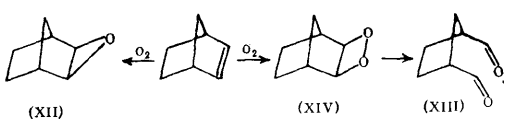


A study of the sensitised photochemical oxidation of norbornene by singlet oxygen at room temperature in different solvents showed[26] that a mixture of the *exo*-epoxide of norbornene (**XII**) and *cis*-cyclopentane-1,3-dialdehyde (**XIII**) is formed in all cases (Table 2).

Table 2. The composition of the products of the photochemical oxidation of norbornene by singlet oxygen in various solvents at room temperature.

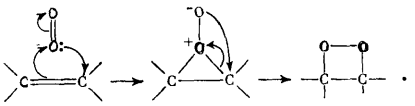
Solvent	Composition of products, %	
	(XII)	XIII)
CH_3CN	39	61
$CH_3COC(CH_3)_3$	53	47
CH_3COCH_3	65	35

The authors[26] believe that the dialdehyde is formed via a dioxetan (**XIV**) stage,

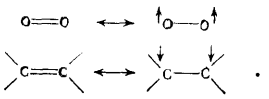


(XII) (XIV) (XIII)

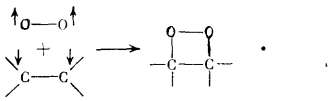
the mechanism of the formation of which can be represented as follows[27,28]:



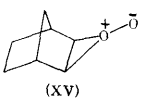
However, we believe that dioxetan can be formed in a different way. In the presence of a sensitiser, the carbon and oxygen double bond systems pass to excited triplet and singlet states[29-31]:



Since the species formed are paramagnetic, the synthesis of dioxetan can be regarded as a homolytic and not a polar interaction:

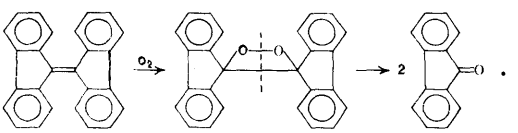


The mechanism of the formation of the norbornene *exo*-epoxide was not finally elucidated[26], but the authors suggest that dioxetan (**XIV**) or the perepoxide (**XV**) may serve as precursors of the epoxide:



(XV)

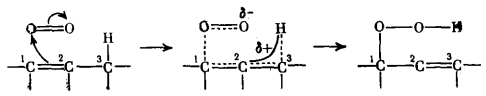
It is noteworthy that the sensitised oxidation of a strained double bond is a general reaction. If the allylic hydrogen atom is inactive and the double bond is highly strained, the dioxetan formed on oxidation may be isolated as a product[27,32,33]. For example, the photochemical oxidation of 9,9'-difluorenylidene, which has a strained double bond, proceeds with formation of fluorenone via an intermediate dioxetan stage[34] in accordance with the following mechanism:



Jefford and Boschung[35] also investigated the photochemical oxidation by singlet oxygen of 2-methylnorborn-2-ene, 2-methylenenorbornane, and their 7,7-dimethyl derivatives in the presence of a sensitiser. They showed that the primary reaction products are not epoxides but unsaturated hydroperoxides. Table 3 lists the relative rates of photochemical oxidation of certain cyclic and bicyclic olefins. The ratios of the rates of *exo*- and *endo*-attack by oxygen on the double bond were calculated for certain bicyclic hydrocarbons from the relative yields of the *exo*- and *endo*-products (Table 4).

The data presented in Tables 3 and 4 indicate a high sensitivity of the photochemical oxidation to steric hindrance: the *endo*-attack by singlet oxygen on the double bond of 2-methylnorborn-2-ene is 1000 times slower than in the reaction involving 1-methylcyclopentene, while the rate of *exo*-attack is reduced approximately by a factor of 250 following the introduction of two methyl substituents in the 7.7-position of 2-methylnorborn-2-ene.

Jefford and Boschung[35] proposed the following mechanism, taking into account the geometry of the transition state in the formation of the hydroperoxide:



(XVI)

and concluded that the transition state (XVI) has a dipolar structure.

Table 3. The relative rates of photochemical oxidation and partial rates of *exo*- and *endo*-attack by singlet oxygen on the double bonds in cyclo- and bicyclo-olefins.

Hydrocarbon	Relative rate of photochemical oxidation	Partial rates	
		of *exo*-attack	of *endo*-attack
	2.3	1.15	1.15
	115.0	57.5	57.5
	9.5	4.5	4.5
	1.0	0.97	0.03
	3.2	3.15	0.05
	0.262	0.108	0.154
	0.077	0.012	0.065

Table 4. The ratios of the rates of *exo*- and *endo*-attack (v_{exo}/v_{endo}) by singlet oxygen on the double bond in bicyclic hydrocarbons[35].

Hydrocarbon				
v_{exo}/v_{endo}	66.0	0.19	28.0	0.67

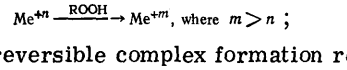
The addition of an oxygen atom to the first carbon atom of the double bond leads to the appearance on the central carbon atom of the allyl fragment of a positive charge δ+, which is delocalised via hyperconjugation with a C–H bond in the α-position relative to the C–C bond. The formation of the hydroperoxide is completed by the transfer of the conjugated γ-hydrogen atom to the O^- centre and the migration of the double bond. The displacement of the double bond in hydrocarbons has been demonstrated with the aid of a deuterium label[35].

III. INTERACTION WITH HYDROPEROXIDES

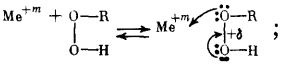
The epoxidation of olefins by reaction with hydroperoxides proceeds in the presence of catalysts. It is recommended that metals whose ions must possess the following fundamental properties be used as catalysts[36]: a high positive charge; vacant electronic orbitals (*d* orbitals) capable of accommodating pairs of electrons; a tendency towards the formation of unstable complexes with the reactants. Such metals are molybdenum, chromium, tungsten, vanadium, manganese, cobalt, niobium, tantalum, titanium, rhenium, selenium, etc.[37] Molybdenum, tungsten, vanadium, and chromium compounds, which may be used as such or with added iron, nickel, manganese, and cobalt are the most common catalysts[38]. The proposed catalysts may be homogeneous and heterogeneous. The most active homogeneous systems comprise molybdenum and vanadium carboxylates and acetylacetonates, alkyl molybdates, and MoO_3 and WO_3 complexes with organic oxygen, nitrogen, and sulphur compounds, etc.[39] Among the catalysts enumerated above, preference is given to molybdenum compounds, which ensure a high selectivity of the epoxidation process[40-42].

A mechanism for the epoxidation of olefins by hydroperoxides in the presence of variable-valence metals has been proposed by Gould et al.[36] and has been confirmed in many investigations[43-50]. On the basis of the above studies, the mechanism of the liquid-phase epoxidation of olefins by hydroperoxides can be represented as follows:

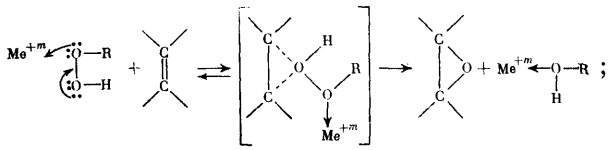
(1) rapid and irreversible activation of the catalyst:



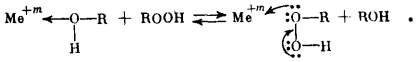
(2) rapid and reversible complex formation reaction:

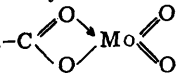


(3) reaction of the complex with the olefin (the stage limiting the rate of the entire process):



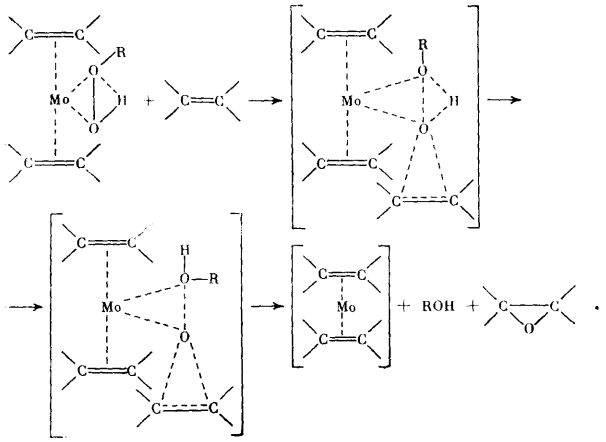
(4) rapid reversible exchange of ligands:



It has been shown[51] that, when ethylphenyl hydroperoxide is added in the oxidation of olefins by the latter in the presence of molybdenum resinate , the valence of the metal changes: molybdenum(V) is converted into molybdenum(VI) and compounds of molybdenum in the +5 and +6 oxidation states (*n* and *m* respectively in the mechanism) exist simultaneously during the epoxidation reaction, and the proportions of the two types of compounds are influenced by the concentration of the epoxidising agent.

In a detailed study of the individual stages of the epoxidation of cyclohexene by ethylphenyl hydroperoxide in the presence of the molybdenum catalyst, it was suggested[52] that the formation of the epoxide proceeds via the reaction

of the hydroperoxide bound in a complex with a new olefin molecule:



It has been found in studies [53,54] by NMR and ESR of the epoxidation of olefins by t-butyl hydroperoxide in the presence of dioxobis(cyclohexane-1,2-diolo)molybdenum that stable paramagnetic free radicals are formed during the reaction and give rise at the beginning to a complex of the catalyst–t-butyl peroxy-radical type and, after the addition of the olefin, a catalyst–t-butylperoxy-radical–olefin complex is formed.

It was shown above that an olefin with a high negative heat of hydrogenation is oxidised at a high rate. In a study of the catalytic epoxidation of individual isomeric butenes by t-butyl hydroperoxide, Farberov and coworkers [55] found that *cis*-but-2-ene is the most reactive. This is consistent with the negative heats of hydrogenation of the relevant hydrocarbons [21] (Table 5).

Table 5. The negative heats of hydrogenation and the reactivities of isomeric butenes in the epoxidation reaction in the presence of molybdenum acetylacetonate (epoxidation temperature 50°C, hydrocarbon concentration 4.0 M, catalyst concentration 1.0×10^{-4} M).

Olefin	$-\Delta H_{hydr}$, kcal mole^{-1}	Rate constant for epoxidation reaction, litre mole^{-1} s^{-1}	Relative rate of epoxidation
But-1-ene	26.8	$0.08 \cdot 10^{-3}$	1.0
trans-But-2-ene	27.6	$1.08 \cdot 10^{-3}$	14.2
cis-But-2-ene	28.6	$2.74 \cdot 10^{-3}$	36.0

It has been shown similarly [56,57] that in the series of cyclic olefins the carbon atom involved in the most strained bond is epoxidised most readily (Table 6). Furthermore, it has been shown by ^{1}H NMR and infrared spectroscopy that, in all cases of the epoxidation of cyclic olefins having double bonds in the ring and in the side chain (vinylnorbornene and vinylcyclohexene), the products are in all cases monoepoxy-derivatives formed on the ring double bond, which indicates a high degree of strain of the latter compared with that of the double bond in the side chain.

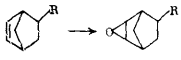
It has been found in the oxidation of norbornene, vinylnorbornene, cyclopentene, cyclohexene, and camphene by t-butyl hydroperoxide in the presence of the molybdenum catalyst [58] that the relative rates of epoxidation of the above hydrocarbons are in the ratios 6.5 : 6.0 : 5.0 : 2.0 : 1 respectively. The opposite dependence of the rate of epoxidation of hydrocarbons on the stretching vibration frequency of the ring C–C bond in the infrared spectra was observed.

Table 6. Degree of conversion of t-butyl hydroperoxide in the epoxidation of cyclo-olefins in the presence of molybdenum acetylacetonate (temperature 0°C, molar ratio olefin : hydroperoxide = 3:1, catalyst concentration 0.001 mole of Mo per mole of hydroperoxide, reaction time 30 min).

Hydrocarbon	Camphene	Vinylcyclohexene	Vinylnorbornene
Conversion of hydroperoxide, wt.%	4.0	21.0	26.5

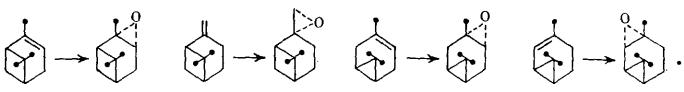
The epoxidation of olefins by hydroperoxides in the presence of catalysts has an electrophilic mechanism [59,60]. Consequently in a series of norbornene derivatives the rate of oxidation should vary as a function of the electronegativity of the substituent. This has been confirmed in a study [61] where it was found that, in the epoxidation of norbornenes by t-pentyl hydroperoxide in the presence of $MoCl_5$, compounds with electron-donating substituents are oxidised at higher initial rates than compounds containing electron-accepting substituents (Table 7).

Table 7. The rates of oxidation of 6-substituted norbornene derivatives by t-pentyl hydroperoxide [61]:



R	CO_2CH_3	$CH_2OCO_2CH_3$	OCO_2CH_3	OH	*exo*-CN	*endo*-CN	Cl	CH_2OH	H	CH_3
10^7W, mole litre^{-1} s^{-1}	2	5	6	7	8	9	15	23	35	116

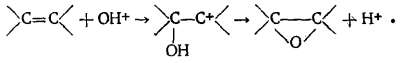
The stereochemistry of the catalytic epoxidation of bicyclic olefins by hydroperoxides has been investigated [60,62] and it has been established that α- and β-pinenes as well as Δ^3- and Δ^4-carenes, which have a markedly hindered double bond, give rise only to the *endo*-epoxides on oxidation by t-pentyl hydroperoxide in the presence of $MoCl_5$, because in all cases there is *endo*-attack on the reactant:



Methods for the determination of the conformations of terpene epoxides by ^{1}H NMR have been developed by Arbuzov et al. [63]

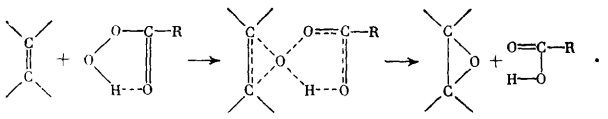
IV. OXIDATION BY PERACIDS

The oxidation of olefins by peracids has been investigated in detail; together with reports containing data on the kinetics and mechanisms of individual reactions, a number of reviews[47,64-66] and monographs[67,68] devoted to the Prilezhaev reaction have appeared in recent literature. It was suggested previously[68,69] that the epoxidising species is the free hydroxyl cation OH^+, which attacks the olefin via the reaction



However, it was found that the Prilezhaev reaction does not undergo general acid catalysis.

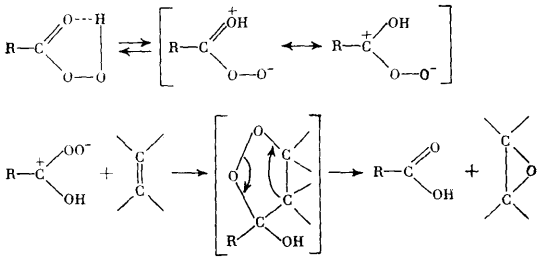
In later studies of the kinetics of the epoxidation of various olefins by peracids[70-73], it was suggested that the epoxide is formed via a π-complex:



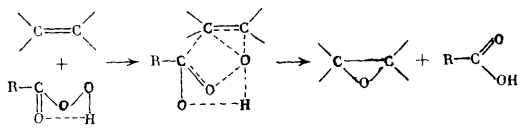
The formation of an intramolecular hydrogen bond in peracids was noted and demonstrated for the first time by Emanuel' et al.[74]

The mechanism of the epoxidation of olefins proposed by Bartlett[70] and Lynch and Pausacker[71] in general agrees satisfactorily with the fundamental process characteristics[67,75]. It explains readily the irreversibility of the reaction and the energetic process characteristics, because the formation of a complex reduces the energy required to abstract an oxygen atom from the peracid and to transfer it to the C=C bond.

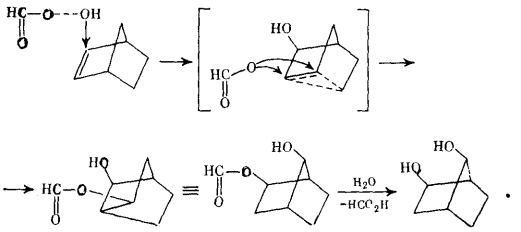
In highly polar solvents, epoxidation via a mechanism involving dipolar 1,3-addition is possible[67,76]:



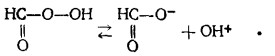
or



A characteristic feature of the Prilezhaev reaction is high stereospecificity leading to pure *cis*-addition of the oxygen atom with retention of the configuration of the substituents at the double bond[67]. However, the bridge structure of bicyclic olefins leads in many instances to an anomalous epoxidation reaction. Thus it was found in one of the early studies[77] that, in the oxidation of norbornene by performic acid, the only product is *cis*-norcamphane-2,7-diol. The authors suggested that the reaction proceeds with a Wagner–Meerwein rearrangement via a stage involving the formation of 2-formyl-7-hydroxynorbornane:

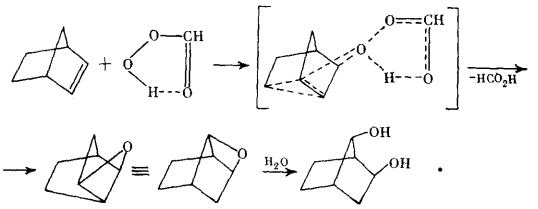


The proposed mechanism is based on the dissociation of performic acid into ions via the reaction



However the HO^+ cation should have a high energy[47] and its formation is not very likely under the given conditions. The intermediate—2-formyl-7-hydroxynorbornane—was not isolated either.

According to modern ideas[67], the oxidation of norbornene by performic acid probably involves a stage in which 2,7-epoxynorbornane is formed:



A study of the epoxidation of norbornene and *exo*-dihydrobicyclopentadiene by perbenzoic acid[78] showed that the reaction proceeds without a Wagner–Meerwein rearrangement and the consequent formation of *exo*-2,3-epoxynorbornane and *exo*-2,3-epoxy-*exo*-5,6-cyclopentanonorbornane respectively (the yield was 80% in both cases). These results were confirmed by Gassman and Pape[79], who oxidised bicyclo[2,2,1]hept-2-ene-7-one and bicyclo[2,2,1]-hept-2-*anti*-7-ol by perbenzoic acid and established that in both cases the reaction also proceeds without a Wagner–Meerwein rearrangement and the consequent formation of *exo*-products: *exo*-2,3-epoxybicyclo[2,2,1]heptan-7-one and *exo*-2,3-epoxybicyclo[2,2,1]heptan-*anti*-7-ol.

endo-Products are formed in the oxidation of norbornadiene by peracids[80-82]. It was shown in the studies quoted that the *endo*-2,3-epoxynorbornene formed undergoes a partial rearrangement which results in the formation of *endo*-bicyclo[3,1,0]hex-2-en-6-al[80,81] or *endo*-9-formylbicyclo[3,1,0]hex-2-ene[82]. The *endo*-pathway of the oxidation of norbornadiene and its homologue is most likely because double bond between the $C_{(5)}$ and $C_{(6)}$ carbon atoms is not shielded by hydrogen atoms[83].

In a study of the stereochemistry of the epoxidation of norbornene and its homologues with subsequent reduction of the products by lithium in ethylenediamine, Brown et al.[84] found that a mixture of *endo*- and *exo*-hydroxy-derivatives is formed in all cases (Table 8). They also demonstrated[84] that the presence of the 7,7-dimethyl substituents in the norbornene molecule decreases the overall rate of epoxidation by a factor of 100 and the rate of *exo*-attack by a factor of 1000; in such cases, the epoxidation proceeds mainly via *endo*-attack on the reactant (Table 8).

A study of the stereoselectivity of the oxidation of olefin double bonds by peracids showed[85] that peroxybenzimidic acid is the least stereoselective reagent in relation to double bonds among other peracids (for example CH_3COOOH). Table 9 presents the relative rates of epoxidation of olefins by peroxybenzimidic and peracetic acids (the rates of reaction of the above acids with cyclohexene were assumed to be unity).

Table 8. The ratio of the amounts of *endo*- and *exo*-products obtained in the epoxidation of norbornene and its homologues by *m*-chloroperbenzoic acid.

Hydrocarbon	Composition of products, %	
	exo-form	*endo*-form
Norbornene	99.0	1.0
7,7-Dimethylnorbornene	12.0	88.0
1-Methylnorbornene	99.0	1.0
2-Methylnorbornene	99.5	0.5
1,7,7-Trimethylnorbornene	5.0	95.0

Table 9. The rates of epoxidation of olefins by peracids.

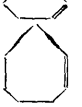
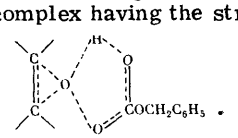
Hydrocarbon	Relative rate of epoxidation		Hydrocarbon	Relative rate of epoxidation	
	by peroxybenzimic acid	by peracetic acid		by peroxubenzimic acid	by peracetic acid
	0.4	0.039		1.46	—
	0.9	1.0			
	1.3	1.0			
	2.1	7.95		0.92	1.43
	3.5	—			
	1.0	1.0		2.03	1.36
				3.8	1.2

Table 10. The yields of *endo*-epoxides in the epoxidation of R-5-norbornenes.

R	Yield of epoxide, %
$COOCH_3$	39
$(CH_2)_2OCOCH_3$	53
$(CH_2)_3OCOCH_3$	39

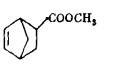
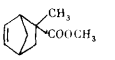
In a study of the oxidation of 5-substituted norbornenes by *o*-benzylmonoperoxycarbonic acid—an extremely effective epoxidising agent yielding mainly *endo*-epoxides—it was found[86] that the reaction gives rise to an intermediate olefin–peracid complex having the structure



(XVII)

This fact constitutes direct confirmation of the mechanism[70,74] of the epoxidation of olefins by perbenzoic acids described above.

Table 11. The oxidation of norbornene derivatives by peracetic acid at 20°C.

Compound	Yield of epoxide, %
	80
	72
	55*
	51

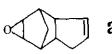
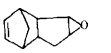
*Under these conditions, dicyclopentadiene gives rise to 30% of the epoxide  and 25% of the epoxide 

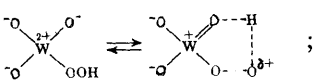
Table 10 presents the yields of the *endo*-epoxides of 5-substituted norbornenes obtained by the reaction of the corresponding hydrocarbons with *o*-benzylmonoperoxycarbonic acid.

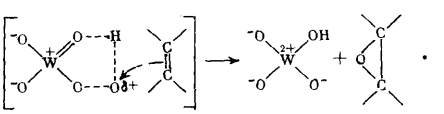
The oxidation of norbornene derivatives by peracetic acid takes place mainly via *exo*-attack on the double bond[87]. The yields of the resulting *exo*-epoxides are listed in Table 11.

V. REACTIONS WITH HYDROGEN PEROXIDE

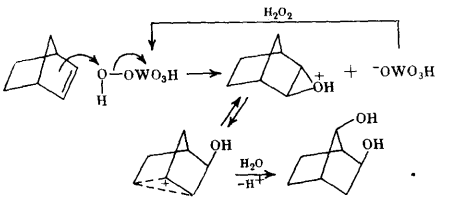
The oxidation of olefins by hydrogen peroxide has been investigated in detail[47]. The reaction is accelerated in the presence of tungstic acid and tungstates. The epoxidation mechanism can be represented as follows[88-90]:

$$HWO_4^- + H_2O_2 \rightleftarrows HWO_5^- + H_2O\ ;$$





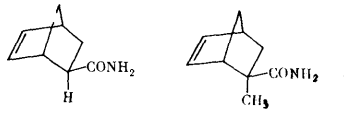
In one of the early papers[91], it is stated that the interaction of norbornene with a solution of hydrogen peroxide in t-butyl alcohol in the presence of tungstic acid yields *exo*, *syn*-norbornane-2,7-diol and not the epoxide. However, the mechanism proposed by the authors includes an epoxide-formation stage:



The occurrence of the rearrangement, caused by the structure of the epoxidised hydrocarbon, constitutes evidence for the cationic mechanism of the addition reaction catalysed by tungstic acid, since the rearrangement is not observed when the corresponding bicyclic radical is formed[92].

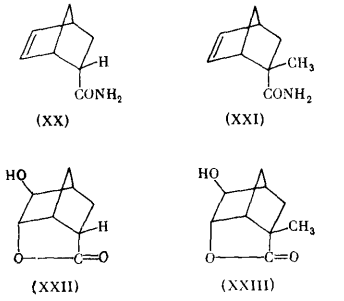
The epoxidation of norbornene hydrocarbons containing functional groups proceeds anomalously. It has been shown[93,94] that, when the functional groups are in the *exo*-positions, the only reaction product is an epoxide. The *endo*-configuration of the carboxy-[93,95], hydroxymethyl[94,96], and methoxycarbonyl[97] groups leads to the complete or partial formation of tricyclic structures containing a heteroatom.

The oxidation of stereoisomeric carbonamides of the norbornene series was investigated in a later study[98]. The authors showed that the oxidation of *endo*-carboxamides (XVIII) and (XIX), containing a strained double bond, proceeds readily with formation of the corresponding epoxides having the *exo*-configuration:



(XVIII) (XIX)

The epoxidation of the stereoisomeric *endo*-carboxamides (XX) and (XXI) leads to the formation of the lactones (XXII) and (XXIII), by virtue of the nucleophilic attack on the carbon atom of the carbonyl group directed towards the positively charged carbon atom in the intermediate complex, formed as a result of the electrophilic attack by the peracid on the norbornene double bond.



(XX) (XXI)

(XXII) (XXIII)

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The review of the literature data on the oxidation of bicyclic hydrocarbons with a bridge bond shows that the oxidation reaction is of theoretical interest, particularly from the standpoint of stereochemistry. Presumably some of these reactions will be used in future in the chemical industry.

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