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Ozonolysis—A Modern Method in the Chemistry of Olefins

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The review is devoted to the advances in the last ten years in the development of the ozonolysis of olefins as a synthetic method, in the study of the structures of peroxy-products of the azonolysis, and in the study of the stereochemistry of ozonides, which have in many respects determined the progress in our ideas concerning the mechanism of the ozonolysis of olefins.
The bibliography includes 351 references.

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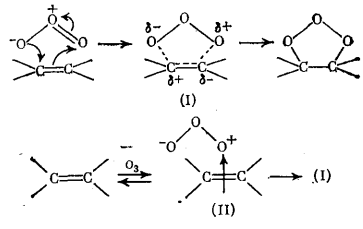
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I. INTRODUCTION

The ozonolysis† of olefins has become not only a recognised analytical method for the determination of the structures of unsaturated compounds, but also a method for the highly selective introduction of oxygen-containing functional groups into the organic molecule at the site of the double bond. The development of the ozone generation technique and of the ozonolysis process itself has attained a level such that this reaction has acquired increasing importance for technology[1]. In recent years the study of the structures of peroxy-products of ozonolysis and of the stereochemistry of ozonides, which has in many respects promoted progress in our ideas concerning the mechanism of the ozonisation of olefins, has been prosecuted particularly vigorously in recent years.

II. PEROXY-PRODUCTS OF OZONOLYSIS AND THE MECHANISM OF THE OZONISATION OF OLEFINS

It has now been established that the ozonolysis of olefins begins with the addition of an ozone molecule to the double bond. The adduct, in which the carbon–carbon bond still persists, has been called the primary ozonide[2] (in this review it is henceforth referred to as the primary ozonide). It is formed via a mechanism involving electrophilic 1,3-dipolar cycloaddition[3] via transition state (I) in which the electrophilic oxygen of the ozone molecule is bound to the carbon atom of the double bond more strongly than the nucleophilic oxygen atom. The interacting ozone and olefin molecules can attain the semipolar transition state (I) either via a single-step concerted cycloaddition[3] or via an additional reversible stage in which the π-complex (II) is formed[4-6]:



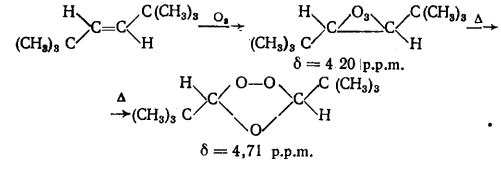
(I)

(II)

†The term "ozonolysis" is used in this review for the entire process involving the cleavage of the double bond by ozone, leading to the final peroxy- or non-peroxy-products. The term "ozonisation" refers only to the action of ozone on an unsaturated compound.

π-Complexes of ozone with aromatic compounds and arylethylenes have been detected by spectrophotometry and ^{1}H NMR at temperatures between −150 and −155 °C.[7,8] Similar complexes have also been observed for the usual olefins[9,10].

The formation of the primary ozonide is an irreversible process occurring with liberation of 37–39 kcal mol^{-1} of heat[11]. The primary ozonide derived from *trans*-1,2-di-t-butylethylene has been detected by ^{1}H NMR at −110 °C and its conversion into the normal ozonide with increase of temperature has been observed[12]:

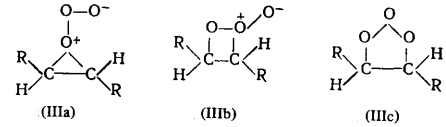


δ = 4.20 p.p.m.

δ = 4,71 p.p.m.

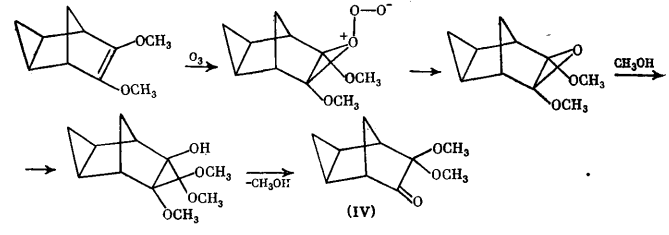
The primary ozonides of other olefins are less stable. The ^{1}H NMR spectra of the primary ozonides of *cis*-olefins recorded at −130 °C contain a broad and poorly resolved signal due to the ring protons in the range 4.35–4.40 p.p.m.[12,13] The greater stability of the primary ozonides derived from *trans*-olefins has been confirmed by quantum-mechanical calculations[14] and microwave spectroscopy[15].

Three probable structures of the primary ozonides have been discussed:



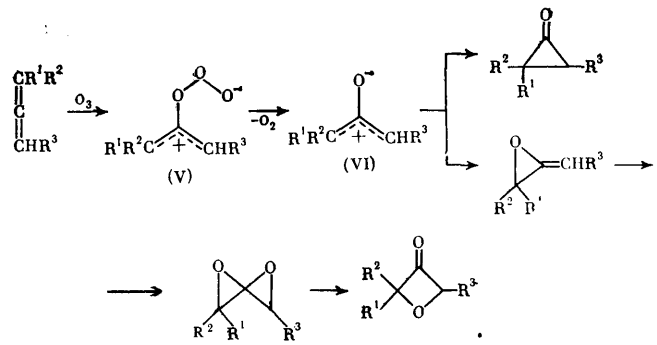
(IIIa) (IIIb) (IIIc)

The formation of the peroxyepoxide (IIIa) or the σ-complex can occur in the ozonisation of sterically hindered olefins, where the reaction products are epoxides[16-18]. The formation of the "anomalous" ozonolysis product (IV) has also been attributed to the formation of the σ-complex[19]:

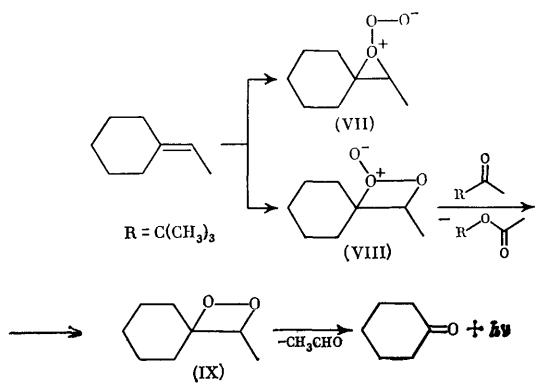


(IV)

In the case of hindered allenes the formation of the initial intermediate (V) as a consequence of the electrophilic attack by ozone has been postulated[20]. The elimination of oxygen leads to the stabilised zwitter-ion (VI), which is converted into the final ozonolysis products:



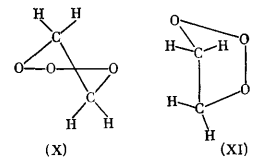
In conformity with the "unifying concept"[21], it has been suggested that the addition of ozone to the double bond of a compound, for example, ethylidenecyclohexane, gives rise to a peroxyepoxide or the σ-complex (VII), which is then converted into the Staudinger four-membered molozonide (VIII), capable of oxidising the excess aldehyde or ketone via a reaction of the Baeyer–Villiger type. The molozonide (VIII) is then converted into the dioxetan (IX) and then into cyclohexanone and acetaldehyde[22,23]:



However, these results were not subsequently confirmed[24–28].

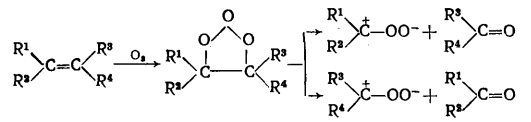
A decisive argument in support of the 1,2,3-trioxolan structure of the primary ozonide (IIIc) rather than that of the molozonide (IIIb) has come from ^{1}H NMR spectra[13,24]. Only one signal due to the methylidyne ring protons has been observed in the spectra of the primary ozonides of symmetrically disubstituted olefins, while in the case of structure (IIIb) these protons would not have been equivalent. Although in the peroxyepoxide (IIIa) both ring protons may also give rise to the same chemical shift, the signal would be significantly displaced downfield as a consequence of the deshielding influence of the positive charge on the neighbouring oxygen atom.

It has been suggested that the carbon–carbon bond in the 1,2,3-trioxolan ring has partial double bond character[29]. Indeed X-ray diffraction yielded a bond length of 1.44 Å, which is the mean of the lengths of single (1.54 Å) and double (1.34 Å) bonds[30]. The low stability of the primary ozonides hinders the study of their conformations by the usual methods. The quantum-chemical calculation, which permitted a choice between the possible half-chair (X) and envelope (XI) conformations of the primary ozonides of lower olefins in favour of the latter as the more stable, proved extremely effective[31]:

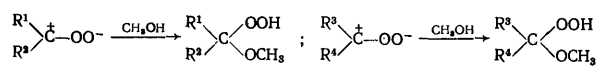


Thus electrophilic 1,3-dipolar cycloaddition of ozone to a carbon–carbon double bond results in the formation of a primary ozonide, which in most cases has the structure of a 1,2,3-trioxolan.

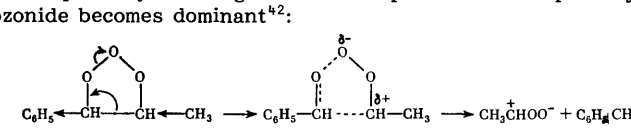
The energy-rich O–O–O linkage and the appreciable ring strain caused by the steric hindrance due to the three neighbouring oxygen atoms are responsible for the low stability of 1,2,3-trioxolan and the ease of its conversion into 1,2,4-trioxolan or the normal ozonide[32]. The mechanism of the conversion of the primary ozonide into 1,2,4-trioxolan has been widely discussed in the last ten years. Up to the middle of the 1960s, Criegee's mechanism[33], which provides a satisfactory explanation of the formation of normal and "cross" ozonides (both monomeric and oligomeric), cyclic dimeric and linear oligomeric peroxides, and "anomalous" ozonolysis products in ozonisation in inert solvents, as well as the formation of α-substituted hydroperoxides in ozonisation in a "participitating" proton-donating solvent of the type HX (X = OH, OR, OCOR, NH_2, NHR, NR_2 or CN), was generally accepted[16,34,35]. A fundamental feature of this mechanism is the formation of a zwitter-ion and of a carbonyl compound as a result of the heterolytic cleavage of the O–O and C–C bonds in the 1,2,3-trioxolan ring of the primary ozonide. For an asymmetric olefin, there is a possibility of two pathways leading to the cleavage of the primary ozonide with formation of different zwitter-ions:



It has been shown in many instances[11,36] that the mode of decomposition of the primary ozonide is determined mainly by the inductive effect of the substituents, while the mesomeric effect plays a secondary role[37]. The mode of the cleavage of primary ozonides can be conveniently investigated by analysing the products of the reaction of the zwitter-ions with methanol, which takes place quantitatively. The α-methoxyhydroperoxides formed correspond to the initial zwitter-ions[38–40]:

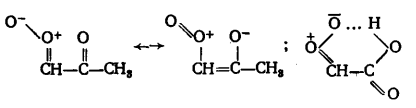


It has been established that electron-donating groups at the double bond promote the formation of a zwitter-ion with the neighbouring carbon atom as a consequence of the decrease of the local positive charge on the latter; correspondingly electron-accepting substituents destabilise the zwitter-ion and facilitate the formation of a carbonyl compound[39,41]. If the substituents exert the same influence, one of the pathways leading to the decomposition of the primary ozonide becomes dominant[42]:

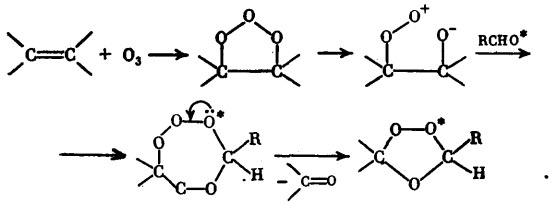


The groups stabilising the zwitter-ion can be arranged in the sequence $CH_3CO > CH_3COOH > C_6H_5 > H > CH_2OH > COOCH_3$. The stabilising influence of the keto-group can be accounted for by the possibility of its participation in the delocalisation

of the charge. The carboxy-group stabilises the zwitter-ion as a result of the formation of a hydrogen bond:

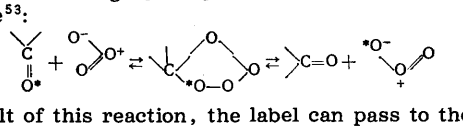


A pathway to the ozonide via a seven-membered cyclic intermediate (XII)—the product of the attack on the primary ozonide by an aldehyde molecule—which constitutes an alternative to the Criegee mechanism, has been proposed[43-46]. The main evidence in support of the new mechanism is the significant incorporation of the ^{18}O label into the peroxide bridge of the ozonide, which has been observed in the ozonisation of *trans*-1,2-di-isopropylethylene and ethylidenecyclohexane with participation of labelled acetaldehyde and propionaldehyde respectively[43,44]:

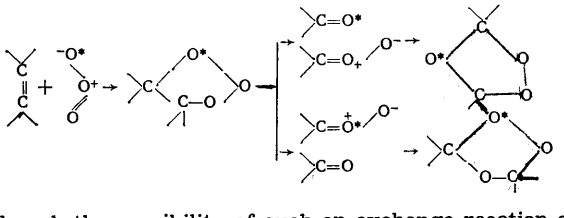


(XII)

The results of the ozonolysis of *cis*- and *trans*-di-isopropylethylenes in the presence of [^{18}O] isobutyraldehyde confirmed the preferential incorporation of the label in the peroxide bridge[47]. However, in the ozonisation of phenylethylenes in the presence of [^{18}O] benzaldehyde[42,48,49] and subsequently also of lower olefins (ethylene, propene, and *cis*- and *trans*-but-2-enes) in the presence of [^{18}O]formaldehyde or [^{18}O]acetaldehyde[50] the label was found exclusively in the ether position in the ozonides. Furthermore, the joint ozonolysis of *cis*- and *trans*-di-isopropylethylene in the presence of [^{18}O]acetaldehyde even at a very low temperature (−110 °C), i.e. under the most favourable conditions for the exchange reaction between the aldehyde and the primary ozonide[52] led to the incorporation of the label in the ether bridge to the extent of 90%. An attempt was made to explain the slight (approximately 10%) incorporation of the ^{18}O label in the peroxide bridge of the ozonide by postulating a reversible exchange [2 + 3] reaction between the aldehyde and ozone[53]:

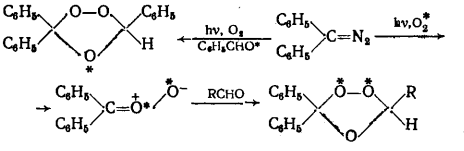


As a result of this reaction, the label can pass to the ozone molecule and with it into any position in the ozonide:

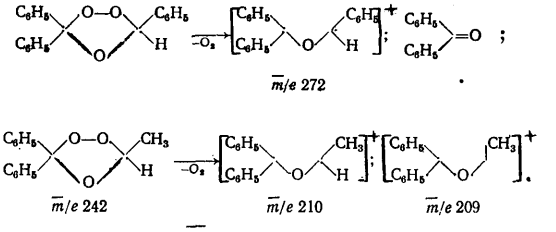


Although the possibility of such an exchange reaction of ozone with the aldehyde cannot be ruled out, under ozonisation conditions it can hardly compete appreciably with the very rapid reaction of ozone with the olefin.

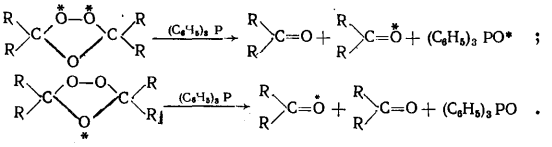
The conflict in the results for the distribution of the ^{18}O label in the ozonide can apparently be accounted for by differences in the methods of analysis. In some investigations[22,45,54] the ozonide was reduced with lithium tetrahydroaluminate with subsequent mass-spectrometric analysis of the resulting alcohols. In other investigations[42,47-49,51] the ozonides were subjected to a direct mass-spectrometric analysis. The method of microwave spectroscopy[15,50] is less susceptible to errors in interpretation, but it is applicable only to the ozonides of lower olefins. For ozonides known to contain the isotope label in the ether or peroxide position, it has been established that the M-32$^+$ fragment ion is formed as a result of the elimination of oxygen from the peroxide bridge of the ozonide. Such ozonides have been synthesised by the photoxidation of diphenyldiazomethane in the presence of benzaldehyde or acetaldehyde[55-58]:



The distribution of the label in ozonides is analysed by employing the molecular ion and the M-32$^+$ fragment[42,48,58]:



Labelled ozonides have been reduced with triphenylphosphine. Mass-spectrometric analysis of the resulting triphenylphosphine oxide showed that the attack is directed exclusively to the peroxide oxygen atom of the ozonide[58,59]:



This indirect method of determining the position of the ^{18}O label in ozonides proved to be the most reliable and convenient. With its aid it has been shown[58] that in the case of di-isopropyl ozonide—the product of the joint ozonolysis of di-isopropylethylene and ^{18}O-isobutyraldehyde—the label is located solely in the ether position, as shown by the absence of ^{18}O from triphenylphosphine oxide.

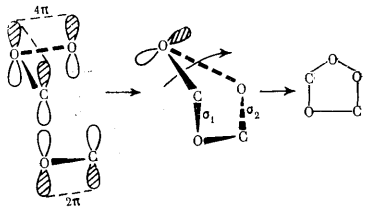
Thus the mechanism of the conversion of the primary ozonide into 1,2,4-trioxolan via the zwitter-ion must be recognised as the only correct one. The Criegee mechanism has been confirmed experimentally by the incorporation of the ^{18}O isotope label exclusively in the ether bridge of the ozonide in the joint ozonolysis of an olefin and the labelled aldehyde.

At the same time the initial Criegee mechanism[4] could not explain the dependence of the ratio of the ozonolysis products (ozonides, aldehydes, and peroxides) on the stereochemistry of the initial olefins[60]. According to Criegee's theory, the geometry of the initial olefin should not have influenced the composition of the ozonolysis product, because the same intermediate is formed from both isomers. Subsequent studies showed that ozonides can exist in the *cis*- and *trans*-forms and that the ratio of both "intrinsic" and "cross" isomers depends on the configuration of the initial olefin[61,62].

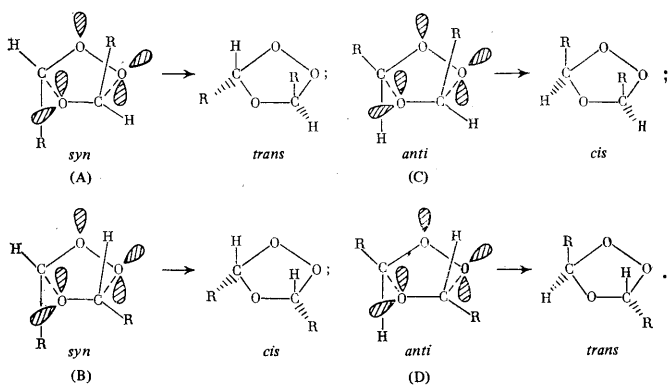
The configuration of a symmetrical disubstituted ozonide is determined by resolving it into its enantiomers. By obtaining one of the optically active forms of one of the isomers

of 3,5-di-isopropyl-1,2,4-trioxolan, it was possible to conclude, for example, that the given isomer has the *trans*-configuration[63], because the *cis*-isomer is a *meso*-form and cannot be resolved into enantiomers. The configurations of a series of isomeric oxonides have been established by their chromatographic separation on acetylcellulose[64,65]. The ratio of the *cis*- and *trans*-ozonides can be determined from ^{1}H NMR spectra, provided that the spectrum of each configuration is known.

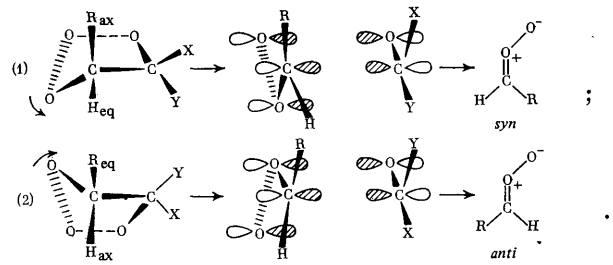
In order to explain the stereospecificity of the formation of ozonides, the existence of the zwitter-ion in the *syn*- and *anti*-configurations has been postulated[66], which was also assumed much earlier by Criegee[67]. Developing this theory, Lattimer et al.[15] considered the cyclodecomposition reactions of the primary ozonide and the cycloaddition of the zwitter-ion to the carbonyl group from the standpoint of the Woodward–Hoffmann theory, according to which ozone and the zwitter-ion are isoelectronic and have a π-system comprising four electrons. Correspondingly the π-systems of the alkene and the carbonyl compound have two electrons. Consequently the reactions involving the formation of the primary and final ozonides can be classified as supra,supra-addition of the 4π- and 2π-systems, which obeys the symmetry laws:



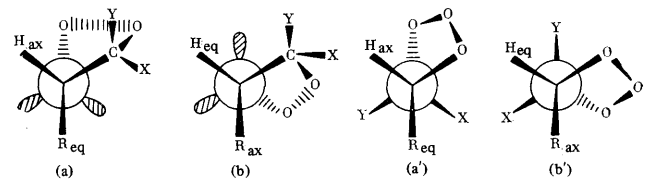
At the instant when the carbonyl group approaches the *syn*-zwitter-ion, the substituents R in the transition state can be oriented in two ways—(A) and (B). The transition state (A) is converted into the *trans*-ozonide and the transition state (B) is converted into the *cis*-ozonide. For the *anti*-zwitter-ion, the transition state model (C) gives rise to the *cis*-configuration of the ozonide and model (D) gives rise to the *trans*-configuration. Evidently models (A) and (C) should be preferable, because the bulky groups of the aldehyde in this case interact less strongly with the free electron pair at the terminal oxygen atom of the zwitter-ion. As a consequence of this, the *syn*-zwitter-ion is converted preferentially into the *trans*-ozonide, while the *anti*-zwitter-ion is converted into the *cis*-ozonide:



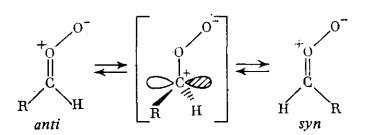
For the decomposition of the primary ozonide into the zwitter-ion and the carbonyl group, it is necessary that the oxygen adjoining the carbon atom converted into the zwitter-ion should be displaced from the "plane" of the ring of the primary ozonide. This transition state has the envelope conformation with axial (pathway 1, leading to the *syn*-zwitter-ion) or equatorial orientation of the substituent R (pathway 2, leading to the *anti*-zwitter-ion):



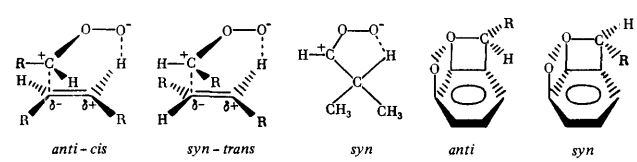
In order to determine which pathway is preferred for a specific olefin, it is sufficient to know the relative stabilities of the two possible transition states. In an estimate of this kind one must take into account the interactions of the substituent with the ring and with another substituent at the neighbouring carbon atom. These interactions are clearly seen in Newman's projection formulae with C–O (formulae a and b) and C–C (formulae a′ and b′) axes:



The zwitter-ion formed can isomerise to a zwitter-ion with the opposite configuration despite its short lifetime[68]:



It is known that specific solvation plays a significant role in the oxidation reactions of organic compounds[69]. It has been noted that the solvent and the olefin can stabilise the zwitter-ion by forming hydrogen bonds[70]. This effect is suppressed by an aromatic hydrocarbon[68], which can form a complex with the zwitter-ion, preventing or retarding its isomerisation:



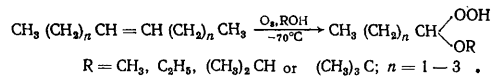
The detection of complex formation and the reversible interconversion of stereoisomeric carbonyl oxides is important for the understanding of the fine structure of the zwitter-ion. Recent calculations[31] showed that both ozone and the carbonyl oxide are singlet biradicals in their ground states. However, there is no experimental evidence for the formation of products of the reactions of the singlet biradical carbonyl oxide. For example, in the decomposition of *trans*-di-t-butyl-1,2,3-trioxolan in cumene or oct-4-ene, which are sensitive to radicals, no radical reaction products were detected[71]. Nor was it possible to detect radicals when the thermal decomposition of the same primary ozonide was followed with the aid of EPR.

Thus the hypothesis of the existence of the zwitter-ion in the *syn*- and *anti*-configurations explains satisfactorily the experimental facts obtained hitherto, including the stereochemical features of the formation of ozonides. The attempt to show that the main intermediate in the ozonisation of olefi is a singlet biradical have not been supported by rigorous experimental data.

III. THE INFLUENCE OF THE STRUCTURE OF OLEFINS AND OZONIZATION CONDITIONS ON THE STRUCTURE OF PEROXY-PRODUCTS OF OZONOLYSIS

The solvent has a decisive influence on the structure of the peroxy-product of ozonolysis. In the ozonisation of olefins in proton-donating solvents (alcohols, carboxylic acids, and water) the zwitter-ion is as a rule stabilised by the addition of a solvent molecule, giving rise to α-substituted hydroperoxides[11,16,72].

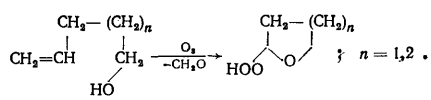
Individual alkoxyhydroperoxides have been isolated from the peroxy-products of the ozonolysis of symmetrical olefins[73]:



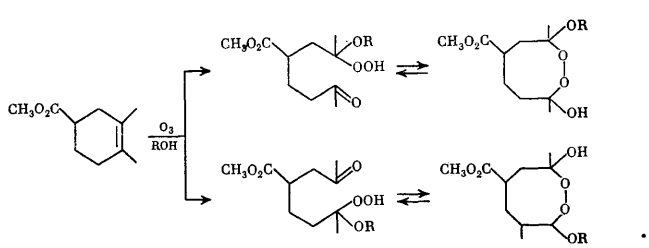
$R = CH_3$, C_2H_5, $(CH_3)_2CH$ or $(CH_3)_3C$; $n = 1-3$.

In the ozonisation of *cis*-octadec-9-ene in various alcohols (C_1–C_{16}) and monocarboxylic acids (C_2–C_{18}) or in an inert solvent containing the same alcohols or carboxylic acids in equimolar proportions, the products are the corresponding α-alkoxy- and α-acyloxy-hydroperoxides[74]. Symmetrical di-(α-hydroxyalkyl) peroxides have been obtained by the ozonisation of α-olefins in aqueous acetone[75].

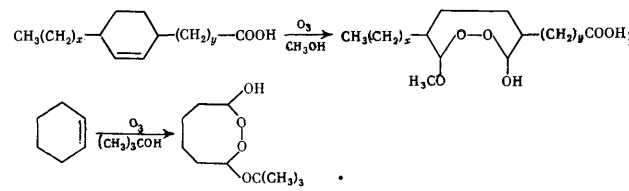
If the proton-donating group is present in the olefin molecule itself, it is involved in the stabilisation of the zwitter-ion[76]. When its position is favourable for the formation of five- or six-membered rings, such stabilisation becomes preferential[77]:



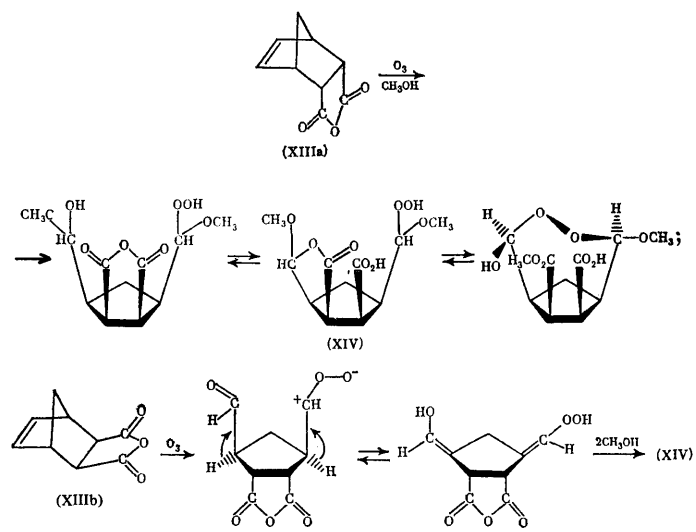
The interaction of the hydroperoxy- and formyl groups leads to the formation of α,α′-disubstituted peroxides. Depending on the nature of the olefin, the products of this reaction can have different structures. Whereas monomeric compounds are formed preferentially from linear olefins[78], in the case of cyclohexene derivatives the main products are oligomeric hemiperacetals[79,80]. However, monomeric cyclic peroxides are formed from cyclohexenes with bulky substituents[81,82]:



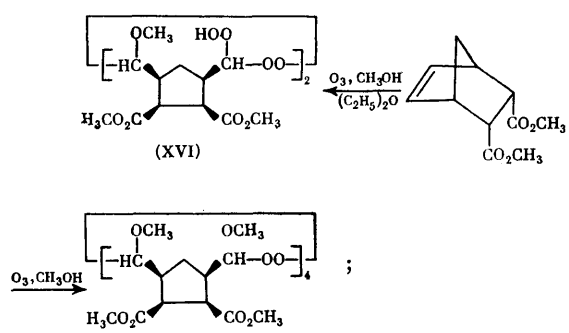
Monomeric α-methoxyhydroperoxides are obtained in the ozonisation of alkylidene- and benzylidene-adamantanes in methanol[83]. The mode of the intramolecular interaction of the hydroperoxy- and formyl groups can be regulated by the presence of bulky substituents next to the double bond[84] or by alcoholic groups[81]:

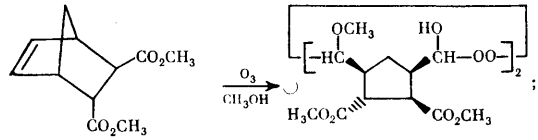


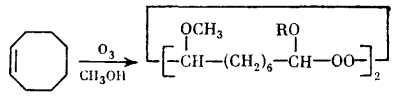
If the formyl and hydroperoxy groups are close together, as, for example, in the ozonolysis product of norbornene[85], then the monomeric hemiperacetal is the main reaction product, while in the ozonisation of carboxy-derivatives of norbornene one obtains exclusively monomeric peroxy-compounds as a consequence of the involvement of the carboxy-groups in the intramolecular interaction[86]. The formation of the same peroxy-product from the *endo*-, *cis*-, and *exo*, *cis*-anhydrides (XIIIa) and (XIIIb) is evidence for the isomerisation of the formyl groups:



On the other hand, in the ozonisation of the dimethyl esters of the stereoisomeric bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids the products are exclusively oligomeric peroxides, the degree of oligomerisation being influenced by the stereochemistry of the methoxycarbonyl groups[87]. The reaction involving cyclo-octene yielded a cyclic bishemiperacetal (XV).[88] If the ozonisation of olefins is carried out in an ethereal solvent, the peroxide ozonolysis products (XVI) and (XVII), with an enhanced content of active oxygen, are formed[87,88]:

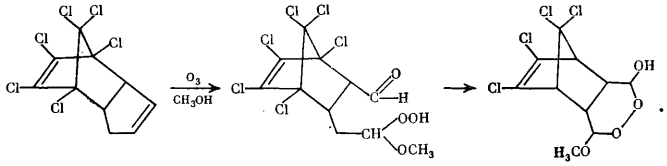




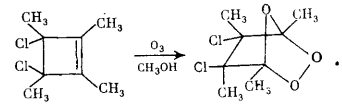


R = H (XV) or OH (XVII).

As a consequence of the deactivation of one of the double bonds by chlorine atoms, hexachlorobicyclopentadiene[89] and hexachlorobicycloheptadiene are attacked by ozone only at the unsubstituted double bond[90]:

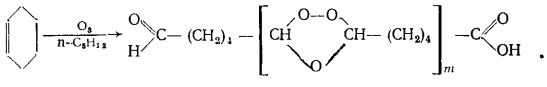


The steric influence can be so great that in the ozonisation of, for example, a substituted cyclobutene in methanol the attack on the zwitter-ion by the solvent is ruled out and the corresponding ozonide is formed[91]:



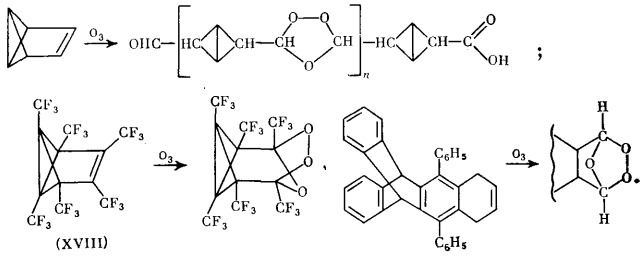
When tetraphenylethylene is ozonised in a mixture of chloroform and methanol, the product is the bishydroperoxide of diphenylmethane instead of the expected methoxyhydroperoxide[92].

The main products of the ozonisation of acyclic olefins in inert solvents are monomeric ozonides[34,93], but oligomeric ozonides are also formed. The yield of the latter depends on the solvent polarity and the structure of the olefin[34,94]. Oligomeric products are obtained almost exclusively from sterically unhindered six-membered olefins[95]:



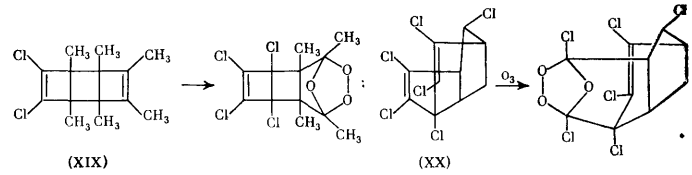
The ozonisation of cyclopentene and cyclobutene gives rise to monomeric ozonides[18,96-98], although the formation of oligomers in this case too has been noted[95].

Oligomeric ozonides are obtained from hexachlorobicyclo-[2,2,1]hepta-2,5-diene[90] and benzvalene[99]. However, the hexakis(trifluoromethyl) derivative (XVIII) gives a high yield of the monomeric ozonide[100]. For steric reasons, monomeric ozonides are also formed from polynuclear hydroaromatic hydrocarbons[101]:



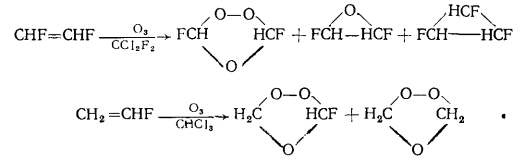
(XVIII)

In the presence of double bonds with electron-donating and electron-accepting substituents [for example, in compound (XIX)] the bond with the higher electron density is attacked[89]. In the polycyclic compound (XX) one of the chloro-substituted double bonds was ozonised[102]:

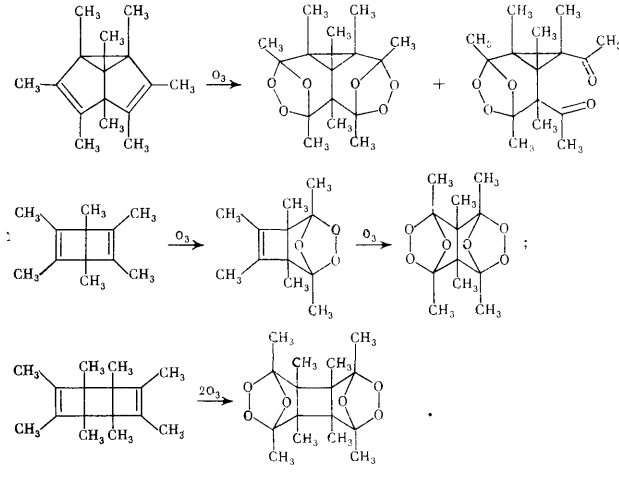


(XIX) (XX)

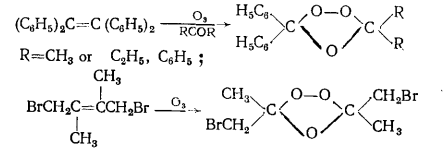
The ozonisation of *cis*- and *trans*-1,2-difluoroethylenes gives rise to a mixture of the ozonide (30%), the epoxide (15%), and trifluorocyclopropane (0.4%),[103] while fluoroethylene yields a mixture of ozonides[104]:



The corresponding diozonides are formed in the ozonisation of octamethylsemibullvalene[96,105], hexamethylbicyclo[2,2,0]-hexa-2,5-diene[106], and octamethyltricyclo-octadiene[107]:

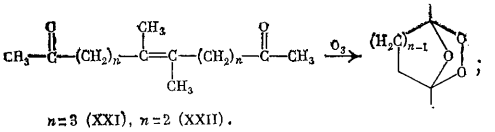


Trisubstituted[108] and tetrasubstituted[109] "cross" ozonides have been synthesised by the ozonisation of appropriately substituted olefins in the presence of an excess of the ketone. If the keto-group, arising on cleavage of the olefin, is activated by an electronegative substituent, then "intrinsic" ozonides are formed in a high yield[110]:



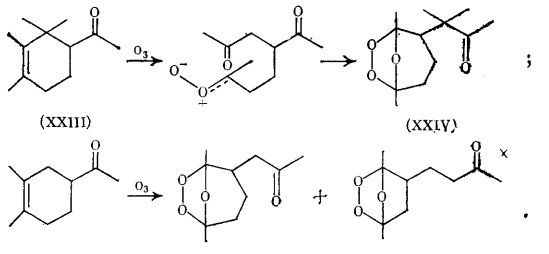
When a keto-group is present in the olefin molecule, there is competition between intramolecular and intermolecular reactions. Thus, in the ozonisation of the diketoalkenes (XXI) and (XXII), the intramolecular reaction of the zwitter-ion

predominates and the ozonides of dimethylcyclopentene and dimethylcyclobutene respectively are formed in high yields[111]:



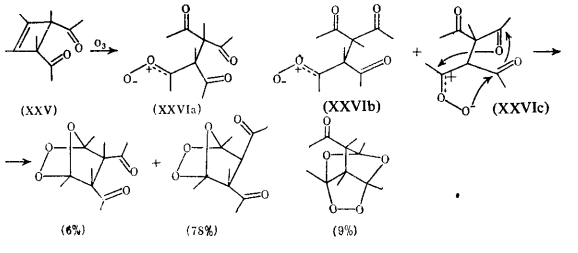
$n=3$ (XXI), $n=2$ (XXII).

In the ozonisation of ketocyclo-olefins intramolecular competition of the two carbonyl groups is observed. Owing to the steric hindrance by the geminal methyl groups in "Dallacker's" ketone (XXIII) only the ozonide of the substituted cyclopentene (XXIV) is formed; in the absence of these methyl groups, the corresponding ozonides of both cyclopentene and cyclobutene are obtained[112]:



(XXIII) (XXIV)

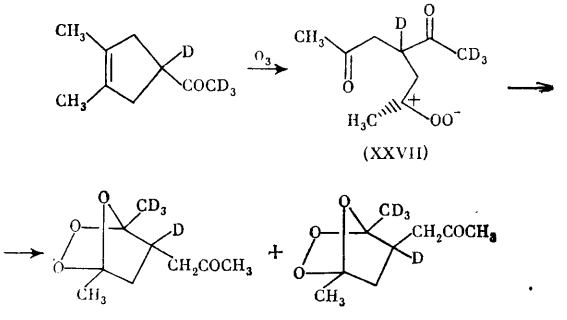
The zwitter-ion formed in the ozonisation of the symmetrically substituted cyclobutene (XXV) can have different conformations (XXVI, a–c), which lead to three products respectively[113]:



(XXV) (XXVIa) (XXVIb) (XXVIc)

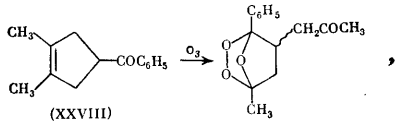
(6%) (78%) (9%)

In the zwitter-ion (XXVII), which contains two acetyl groups, there is interaction with the nearest acetyl group, because this leads to the more stable ozonide of cyclobutene[26]:

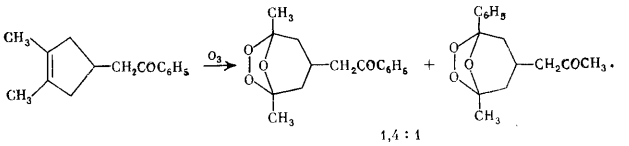


(XXVII)

For the same reason, in the ozonisation of compound (XXVIII) the reaction of the zwitter-ion with the benzoyl group and not with the more reactive acetyl group takes place preferentially. If the carbonyl groups are located in equivalent positions, the acetyl group is the more reactive[26]:

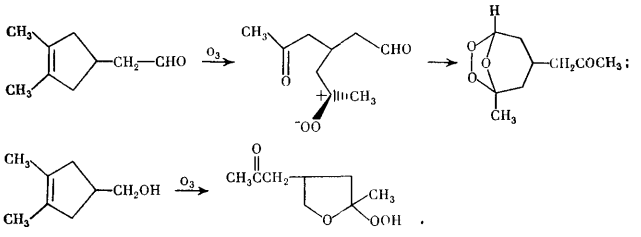


(XXVIII)

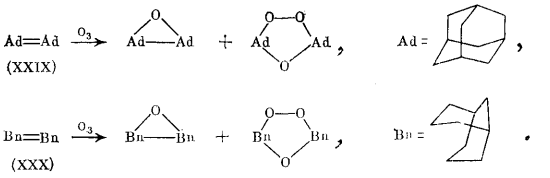


1,4 : 1

If a formyl or hydroxy-group is present, the zwitter-ion reacts with them and not with the acetyl group[26]:

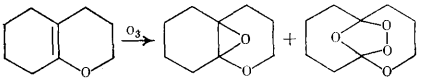


Sterically hindered olefins give rise to epoxides as well as ozonides. In the ozonisation of the alkenes (XXIX) and (XXX) the corresponding epoxides are formed preferentially instead of the expected methoxyhydroperoxides even in the presence of methanol[114]:

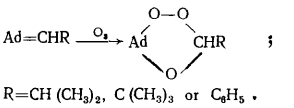


(XXIX) (XXX)

An analogous behaviour has been observed in the ozonisation of tetrahydrochromone[115]:

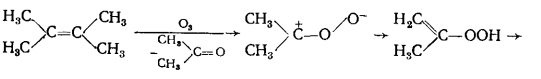


The steric hindrance may be so great that the double bond becomes inert towards ozone. Thus, whereas isopropyl-, t-butyl-, and phenyl-methyleneadamantanes normally give rise to ozonides, the replacement of the vinyl hydrogen atom by the t-butyl or phenyl group makes these compounds resistant to ozone[114]:

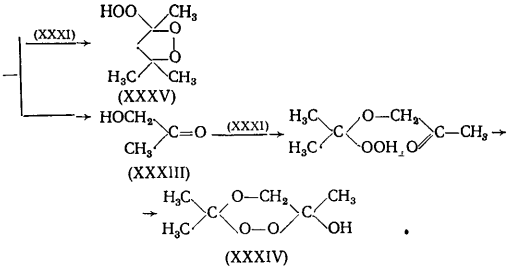


R=CH $(CH_3)_2$, C $(CH_3)_3$ or C_6H_5.

Certain zwitter-ions can be stabilised by isomerisation or rearrangement, which leads to anomalous peroxide or non-peroxide ozonolysis products. Thus the zwitter-ion (XXXI), formed in the ozonisation of tetramethylethylene, isomerises to the α-hydroxyketone (XXXIII) via the vinyl hydroperoxide (XXXII). This results in the formation of the six-membered trioxan (XXXIV) [109] or the cyclic hydroperoxide (XXXV):[116]

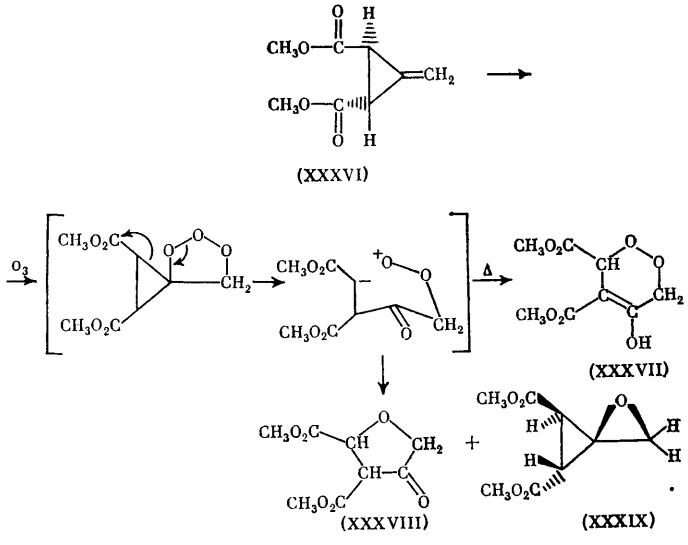


(XXXI) (XXXII)



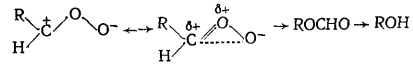
(XXXV) (XXXIII) (XXXIV)

The ester of Feist's acid (XXXVI) is ozonised anomalously, being converted into a mixture of compounds (XXXVII)–(XXXIX). Evidently the peroxide (XXXVII) is the isomerisation product of the zwitter-ion[117]:

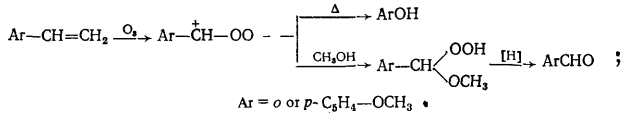


(XXXVI) (XXXVII) (XXXVIII) (XXXIX)

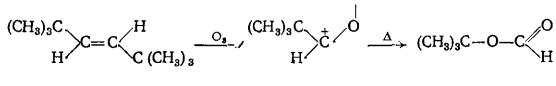
Anomalous ozonolysis products are usually observed when the zwitter-ion contains a group with a tendency towards migration[16]:



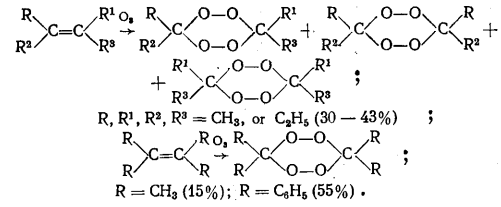
Such rearrangements are characteristic of zwitter-ions generated from substituted styrenes[118]. On the other hand, if the zwitter-ion is bound by methanol, anomalous products are not formed[119]:



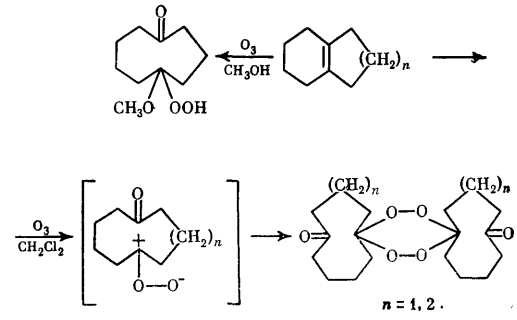
Alkyl groups show a much smaller tendency towards migration. In the ozonisation of even *trans*-di-t-butylethylene only 5% of t-butyl formate is formed[118]:



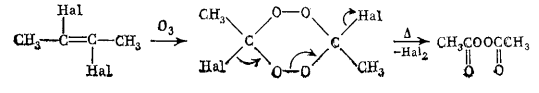
When the reaction is carried out in inert solvents, the formation of dimeric and oligomeric peroxides together with ozonides is frequently noted[32,110,120]. The yield of these compounds depends greatly on the structure of the olefin. Thus, whereas in the ozonisation of α-olefins only traces of dimeric peroxides are formed[11,16], dimeric normal and cross peroxides are obtained from tetrasubstituted ethylenes in yields ranging from 15 to 55%.[121]



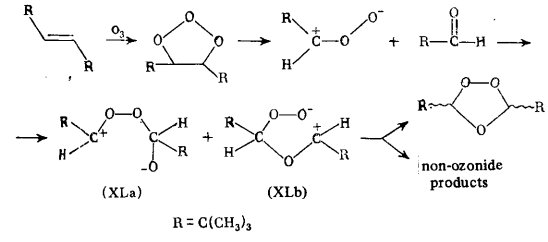
The dimerisation of the zwitter-ion derived from 4,5,6,7-tetrahydroindan[122] and 9,10-octalin[123] leads to the corresponding cyclic diperoxides. The dimerisation does not occur when the ozonisation is carried out in methanol[122]:



Diacetyl peroxide is obtained from *trans*-2,3-dibromobut-2-ene, probably via an intermediate cyclic diperoxide[124]. The crystalline dimeric α-chloroperoxide has been isolated in the reaction of the dichloro-derivative[125]:

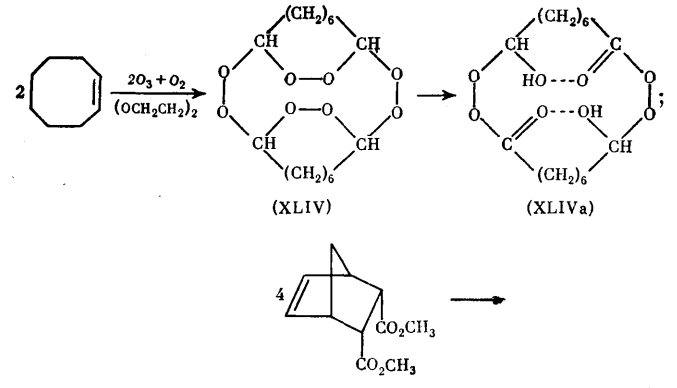


The influence of the solvent on the formation of ozonides has been studied in detail in relation to *trans*-di-t-butylethylene[71]. It has been shown that the ozonide is formed only in non-polar solvents (hydrocarbons), while in methylene chloride, trichlorofluoromethane, acetone, and ethyl acetate it is not formed at all. Ozonisation in diethyl ether at −75 °C does not give rise to the ozonide, but at a lower temperature (−90 °C) it is possible to obtain the ozonide in 25% yield. The addition of an extraneous aldehyde reduces the yield of both the normal and "cross" ozonides. These results have been explained by the stepwise recombination of the zwitter-ion and the aldehyde. In a non-polar solvent the intermediate (XLa) [71] or (XLb) [126] cyclises to the ozonide, while a polar solvent solvates it, increasing the lifetime and probability of side reactions (reactions with the carbonyl oxide and aldehyde as well as polymerisation)[71]:

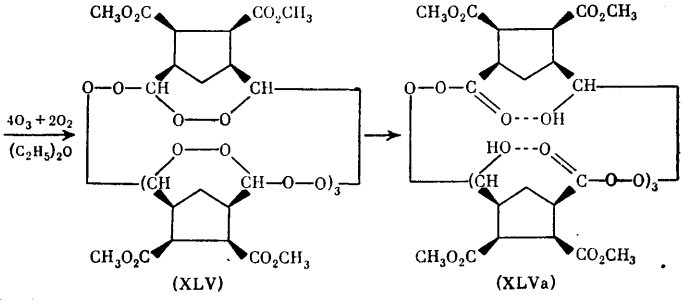


(XLa) (XLb) non-ozonide products

An oligomeric intermediate of type (XLa) or (XLb) solvated by a polar ethereal solvent can undergo further oxidation, which in the ozonisation of cyclic olefins leads to the peroxide ozonolysis products (XLIV) and (XLV),[88,127] which isomerise to the α-hydroxyperesters (XLIVa) and (XLVa):



(XLIV) (XLIVa)



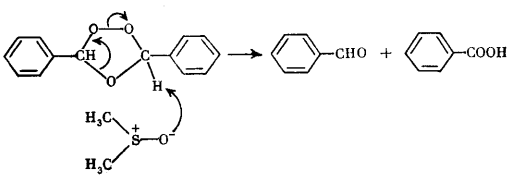
(XLV) (XLVa)

IV. REACTIONS OF PEROXY-PRODUCTS OF OZONOLYSIS

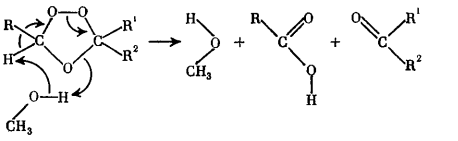
In the ozonisation of olefins a degree of oxidation intermediate between an aldehyde and carboxylic acid is attained. The reactions of ozonides and other peroxy-products of ozonolysis can be divided into two types: those occurring without a change in the degree of oxidation attained (cleavage reactions) and those with a change in the degree of oxidation (oxidation and reduction reactions).

The mode of decomposition of peroxy-compounds depends significantly on the nature of the solvent[69]. The acidity of the medium also influences hydrolysis, solvolysis, alcoholysis, and acidolysis.

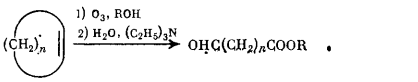
The usual products of the cleavage of ozonides are the corresponding aldehydes and carboxylic acids[16,34]. In an aqueous medium ozonides are cleaved with difficulty[16], but under the influence of strongly solvating solvents (dimethyl sulphoxide, dimethylformamide, and amines) the fragmentation of stilbene ozonide proceeds rapidly and quantitatively[128]:



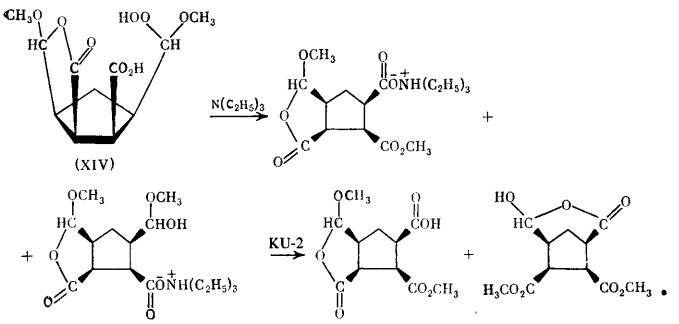
In methanol and benzyl alcohol the rate of fragmentation of ozonides is significantly higher than in benzene, di-isopropyl ether, dioxan, and tetrahydrofuran[65,129]. The solvolysis of ozonides proceeds at identical rates in neutral and weakly acid media, while in an alkaline solution the process is accelerated. The isotope effect observed in the methanolysis of deuterated ozonides[65] shows that the stage involving the elimination of a proton from the trioxolan ring is rate-determining. The exceptional role of the alcohol in the fragmentation of ozonides can be explained by the fact that it behaves simultaneously as a "base" and an "acid"[65]:



α-Substituted hydroperoxides are cleaved more readily than ozonides[130]. Thus the hydrolysis of alkoxyhydroxyperoxides derived from cyclic olefins gives rise to the esters of the corresponding ω-formylcarboxylic acids in 85% yield[131]:

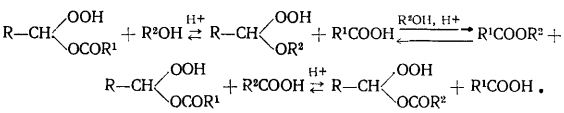


The isomerisation of the hydroperoxy-group to the carboxylate group has been observed in the interaction of the peroxide (XIV) with triethylamine[86]:

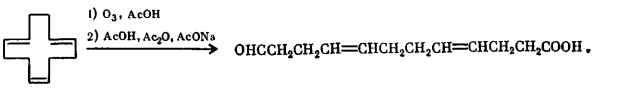


(XIV)

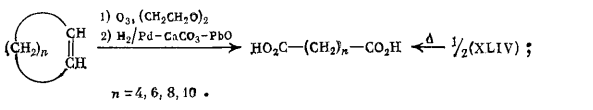
α-Acyloxyhydroperoxides undergo transesterification[132]:



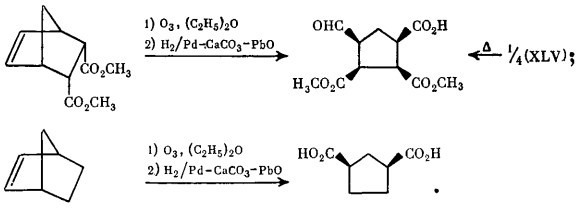
The acidolysis of the product of the controlled ozonolysis of cyclic polyolefins in acetic acid leads to unsaturated ω-formylcarboxylic acids[133]:



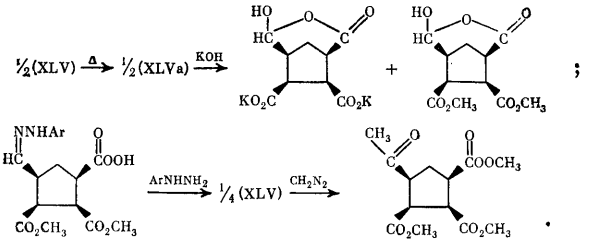
The isomerisation and cleavage of peroxides with a high content of active oxygen, which are formed in the ozonisation of cyclo-olefins in ethereal solvents[88], leads to the corresponding α,ω-dicarboxylic acids, which constitutes a new method of synthesising carboxylic acids without the need for an additional oxidation stage after ozonisation[134-136]:



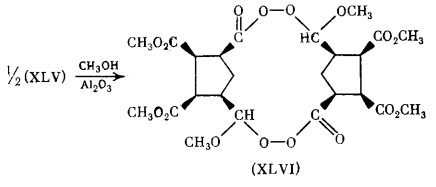
The fragmentation of the peroxide (XLV) yields the corresponding formylcarboxylic acid, while the ozonolysis of 2-norbornene in an ethereal solvent results in the formation of *cis*-cyclopentane-1,3-dicarboxylic acid[127]:



The fragmentation of the peroxide (XLV) also takes place in an alkaline solution and its interaction with diazomethane or 2,4-dinitrophenylhydrazine leads to the formation of peracid groups[127]:

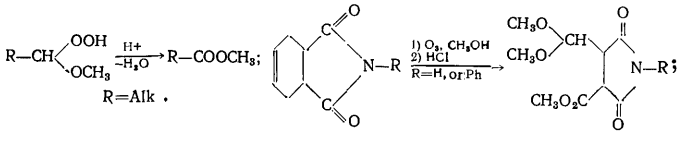


On being eluted with methanol from alumina, the tetrameric peroxide (XLV) is converted[127] into the dimeric α-methoxyperester (XLVI):

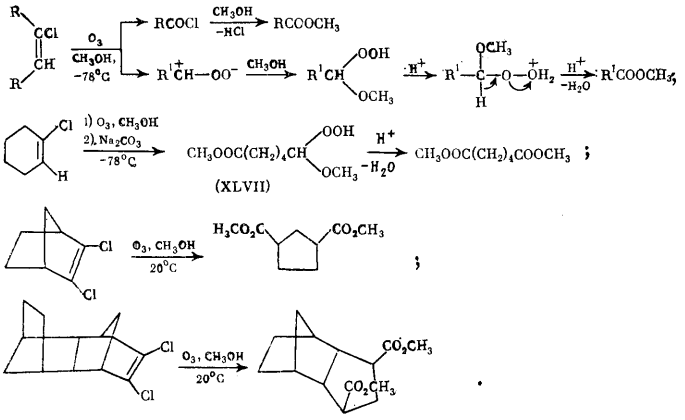


(XLVI)

Alkoxyhydroperoxides derived from trisubstituted and asymmetrically disubstituted olefins hydrolyse rapidly to the corresponding ketones and alcohols[137]. Peroxides obtained from symmetrically disubstituted olefins do not give high yields of aldehydes under these conditions. Treatment with hydrogen chloride converts methoxyhydroperoxides quantitatively into the methyl esters of the corresponding carboxylic acids[138]. Derivatives of ω-formylcarboxylic acids have been obtained under these conditions from certain cyclic olefins[139]:

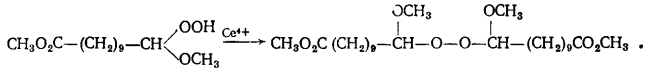


The peroxides formed in the ozonisation of chloro-olefins in methanol readily decompose into the corresponding methyl carboxylates. By neutralising the hydrogen chloride evolved, it is possible to isolate the methoxyhydroperoxide (XLVII):[138,140]



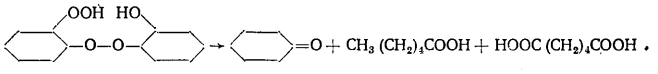
(XLVII)

Oxidation of α-alkoxyhydroperoxides with cerium ammonium nitrate leads to the crystalline dialkoxyperoxides[129]:

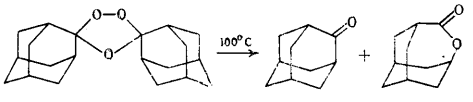


As in hydrolysis, the main products of the thermal decomposition of ozonides are the corresponding aldehydes and carboxylic acids[1,11,141].

When α-hydroperoxy-α-hydroxydicyclohexyl peroxide is heated in boiling toluene, cyclohexanone is formed preferentially (25%) and there are lower yields of caproic (8%) and adipic (4%) acids[28]:

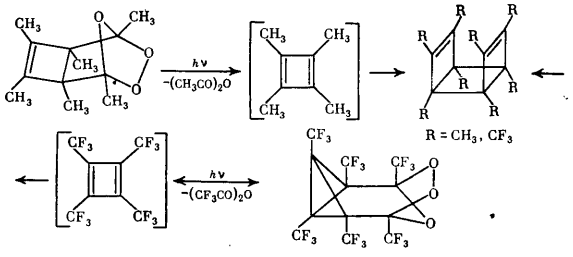


Thermal, and recently also photochemical, cleavage of ozonides has become a promising trend in organic synthesis[142]. Thus the thermolysis[96,142] of bisadamantylidene ozonide leads to the formation of adamantanone and the lactone (XLVIII):[114]

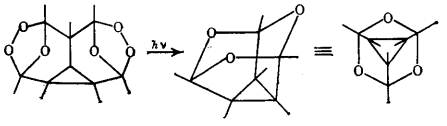


(XLVIII)

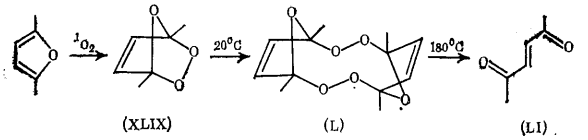
The photolysis of the mono-ozonides of Dewar hexamethylbenzene[143] and hexakis(trifluoromethyl)benzvalene[100] leads to the *syn*-dimers of tetramethyl- and tetrakis(trifluoromethyl)-cyclobutadiene:



The photolysis of the diozonide of octamethylsemibullvalene results in the formation of a triketal of a new type[103]:

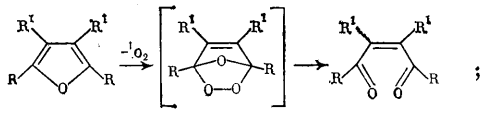


Ozonides can be synthesised by methods other than the ozonisation of olefins[120]. The method involving the oxidation of furan derivatives with singlet oxygen[144], which can be readily obtained, for example, from the adduct of ozone with triphenyl phosphite[145,146] or with certain other compounds[147], is of special interest. The [4 + 2] cycloaddition results in the formation of the mono-ozonides of substituted cyclobutadienes[142]. Thus the photoxidation of 2,5-dimethylfuran yields the ozonide (XLIX), which is converted at room temperature into the stable dimer (L), the latter decomposing into the dione (LI) only at a high temperature[144]:



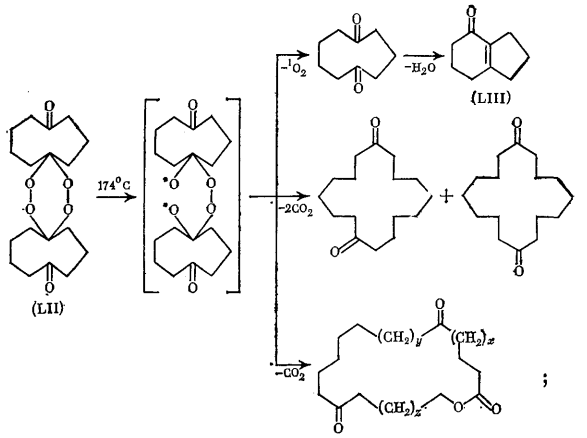
(XLIX) (L) (LI)

The photoxidation of substituted furans can be regarded as a general method of synthesis of *cis*-diacylolefins[142]:



R = R¹ = H; R = R¹ = C_6H_5; R = CH_3, R¹ = H; R = C_6H_5, R¹ = H .

The thermolysis and photolysis of cyclic di- and tri-peroxides have been considered in reviews[142,148]. Such peroxides are usually synthesised by the reaction of cycloalkanones with hydrogen peroxide[149]. In the ozonolysis of certain olefins they are formed as a consequence of the dimerisation of the zwitter-ion. The thermal or photochemical fragmentation of cyclic diperoxides leads to carbocyclenes, lactones, and cyclic ketones[142]. Thus the diperoxide (LII), obtained by the ozonolysis of 4,5,6,7-tetrahydroindan, is converted on heating in boiling decane into cyclononane-1,5-dione (18%), [cyclising to compound (LIII) during isolation], a mixture of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione (50%), and four isomeric dioxoheptadecanolides (16%):[122]



(LII) (LIII)

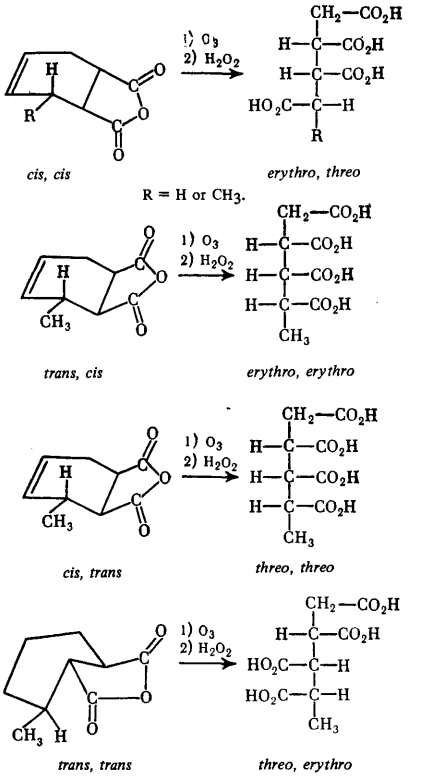
x = 1, y = 3, z = 1; x = 1, y = 2, z = 2; x = 2, y = 2, z = 1; x = 2, y = 1, z = 2 .

The reactions of ozonolysis peroxy-products under the influence of oxidants or reductants are widely used in preparative organic synthesis[16,34,150] and have already found application in industrial technology[1,151]. The oxidative decomposition of peroxy-products of ozonolysis takes place in two stages: the oxidation proper and thermal decomposition of peroxides. In the synthesis of carboxylic acids the two stages are combined or are arbitrarily divided in terms of temperature conditions#.

Oxidative decomposition occurs under the influence of oxygen at an elevated temperature. In this case oxidation initiators or catalysts (ozone, variable-valence metal compounds[1,16,153–159], inorganic salts in polar aprotic solvents[160], and aminoacids[161]) are used. The oxidants consist of a suspension of silver oxide in an alkaline solution[1,34,35], potassium permanganate[162], chromic acid[163], and nitric acid[164]. However, hydrogen peroxide usually employed as a mixture with formic or acetic acid, is the most convenient and most widely used reagent[1,35,150,165–167]. Investigators have paid particular attention to the synthesis of aliphatic α,ω-dicarboxylic acids[168,169], which are of greatest practical interest[1,170,171]. Methods combining the ozonisation and oxidation stages have been developed[1,35,172].

The ozonolytic synthesis of polycarboxylic acids and other polyfunctional compounds has been studied to a lesser degree. When the molecule contains several functional groups, they interact and complicate the oxidative decomposition. In the ozonolysis of cyclic polyenes or cyclo-olefins containing functional groups, catalysts increasing the process selectivity are therefore used.

The isomeric butane-1,2,3,4-tetracarboxylic[174–176] and pentane-1,2,3,4-tetracarboxylic[177,178] acids have been synthesised by the ozonolysis of the stereoisomeric Δ^4-tetrahydro- and 3-methyl-Δ^4-tetrahydro-phthalic acids[173]:



cis, cis — *erythro, threo*

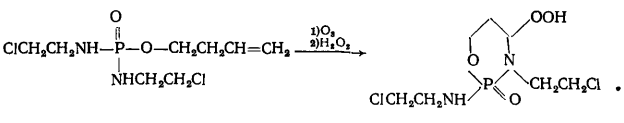
R = H or CH_3.

trans, cis — *erythro, erythro*

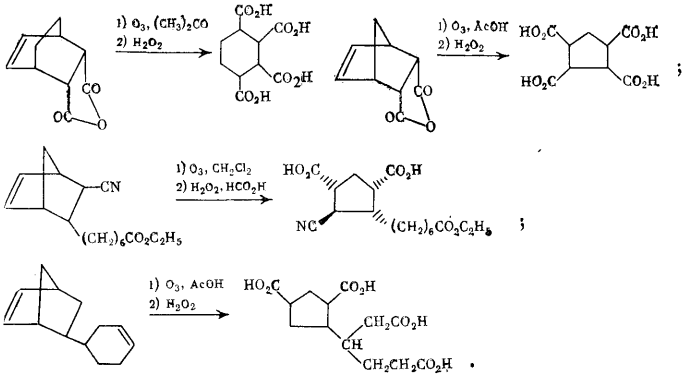
cis, trans — *threo, threo*

trans, trans — *threo, erythro*

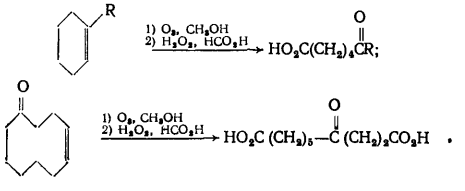
#In the ozonolysis of the alkenyl esters of phosphorodiamidic acids, peroxy-compounds were isolated after the first oxidative decomposition stage[152]:



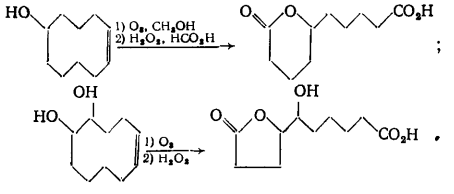
Cyclic polycarboxylic acids have been obtained from derivatives of bicyclic olefins[179–181] and tricarboxylic acids have been synthesised from alkenylcyclohexenes[182]:



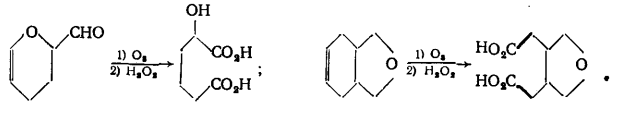
Ketocarboxylic and ketodicarboxylic acids have been obtained by the oxidative ozonolysis of 1-alkylcycloalkenes[183] and cycloalkenones[184] respectively:



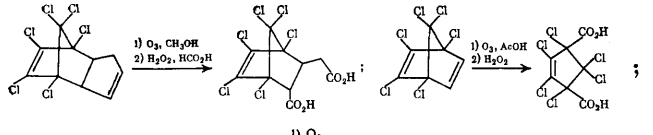
The ozonolysis of cyclo-olefins containing a hydroxy-group led to lactones whose hydrolysis constitutes a pathway to hydroxydicarboxylic acids[185,186]:

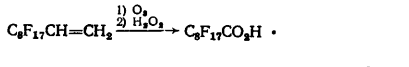


An α-hydroxydicarboxylic acid has been obtained from the acrolein dimer[187], while tetrahydrofuran derivatives have been synthesised from a cycloalkene condensed with a heterocycle[188]:

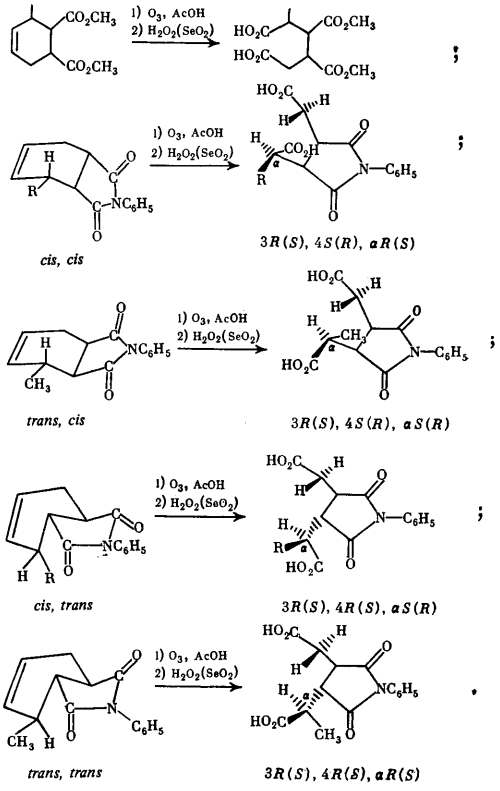


In order to synthesise polychloro-[89,90,189] and polyfluoro-derivatives[190] of di- and mono-carboxylic acids, the corresponding halogeno-derivatives of olefins have been ozonised:

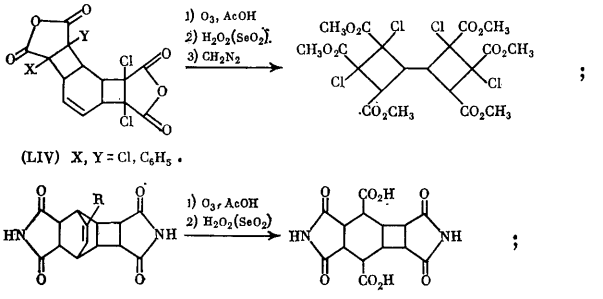




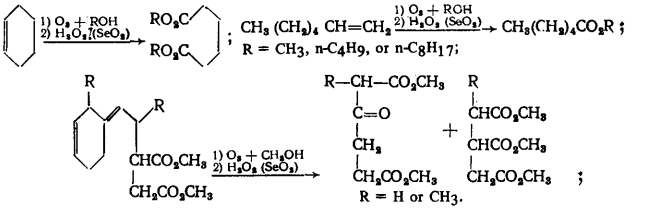
The oxidative decomposition of peroxy-products of ozonolysis, carried out by treatment with hydrogen peroxide, can be accelerated with the aid of selenium dioxide[191–193], in the presence of which the process proceeds under milder conditions with a higher selectivity. This makes it possible to increase the yield by 10–30% as well as the purity of the aliphatic polycarboxylic acids. Thus the 2,3-dimethyl ester of pentane-1,2,3,4-tetracarboxylic acid[191–193] and the corresponding stereoisomeric 3,4-disubstituted *N*-phenylpyrrolidine-2,5-diones[194–196] have been synthesised from the dimethyl ester and the stereoisomeric *N*-phenylimides of Δ^4-tetrahydrophthalic acid and its 3-methyl derivative:



The use of selenium dioxide permitted the successful ozonolysis of the polycyclic compounds (LIV) and (LV):[197,198]

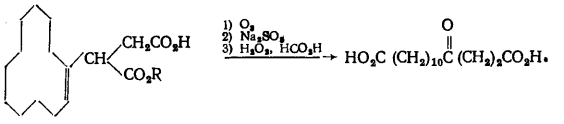


The oxidative decomposition of the peroxy-products of the ozonolysis of olefins in the corresponding alcohols led to the formation of carboxylic acid esters[193,199,200]:

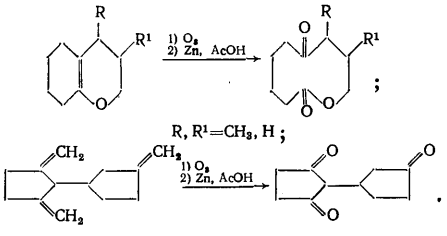


The copolymers of butadiene with isobutene[150,201,202] and styrene[203] have been converted by oxidative ozonolysis with participation of pyridine into the corresponding oligomers with terminal carboxy-groups. 3-Phenyladipic acid has been synthesised by the selenium dioxide-catalysed oxidative decomposition of the peroxy-product of the ozonolysis of regular butadiene–styrene rubber[204,205].

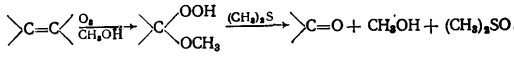
The peroxy-products of ozonolysis are sometimes subjected to preliminary reduction in order to facilitate the oxidative decomposition[206]:



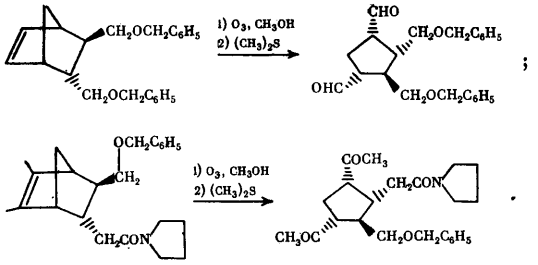
Various reductants, used to convert the peroxy-products of ozonolysis into aldehydes and ketones, have been listed in a number of reviews[16,34,207]. Among traditional reagents, sodium bisulphite[208], the lower-valence metal salts[209–211], alkali metal iodides[212], and sodium thiosulphate[213,214] have been used in recent years. Among inorganic reductants, zinc dust has been most often employed[215–219], for example, in the reductive ozonolysis of tetrahydrochromone derivatives[220] and the cyclo-oligomers of allene[221]:



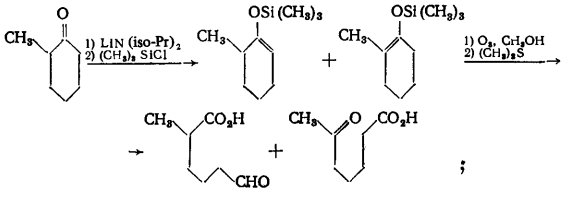
Organic reductants have been used on an increasingly wide scale in recent years. Dimethyl sulphide[222–224] and sometimes other dialkyl sulphides or thiacyclanes[225,226] have been used to synthesise alkoxyhydroperoxides:

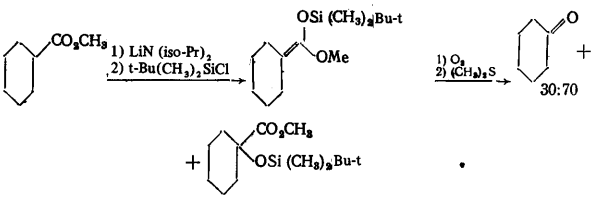


Dimethyl sulphide has been introduced into practical fine organic synthesis[227–230], for example, the synthesis of the intermediates for prostaglandins[231,232]:

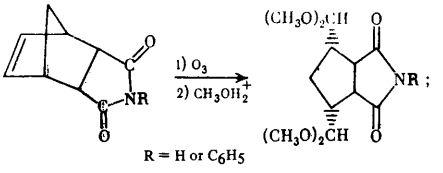


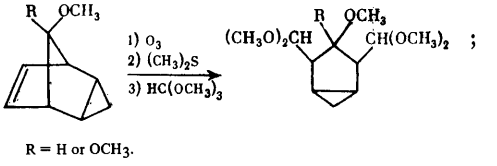
Ozonolysis has found an interesting application for the cleavage of ketones and carboxylic acids via the trimethylsilyl ethers of their enolic forms[233]:



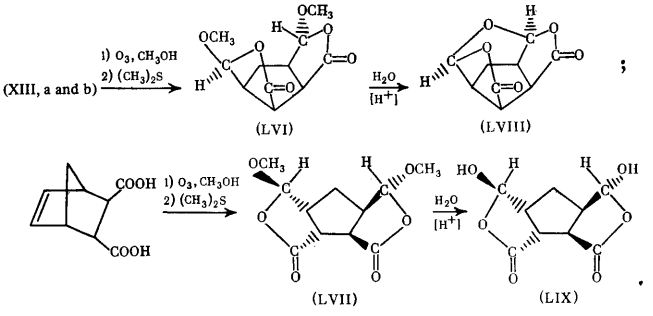


Aldehydes can sometimes be more conveniently isolated in the form of acetals[139,234–236]:

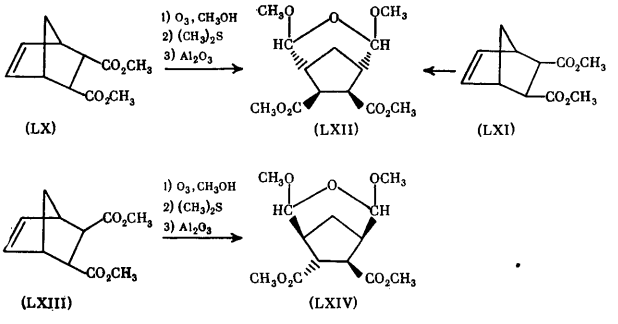




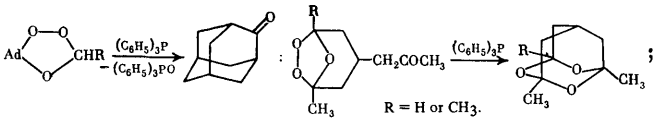
Under the influence of dimethyl sulphide, the peroxy-products of the ozonolysis of the *endo*-, *cis*- and *exo,cis*-anhydrides (XIII, a and b) give rise to the same *syn*-3,5-bis-(methoxymethyl)dilactone (LVI), while the *endo,exo*-diacid gives rise to the *anti*-isomer (LVII) under analogous conditions[237]. In the presence of water both the ozonolysis peroxy-products and the dilactones (LVI) and (LVII) are converted into oxygen-containing polyheterocyclic compounds (LVIII) and (LIX) respectively[86,237]:



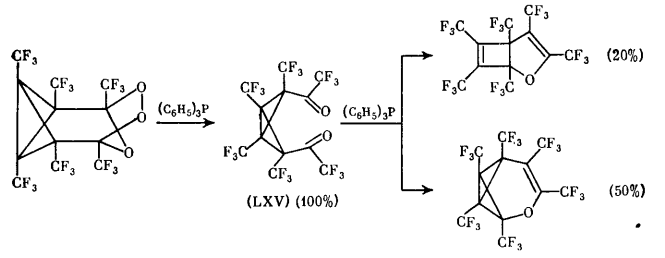
The peroxy-products of the ozonolysis of the *endo,cis*- and *exo,cis*-diesters (LX) and (LXI) are converted on treatment with dimethyl sulphide into the same product (LXII), while the isomeric compound (LXIV) is formed under analogous conditions from the *endo,exo*-isomer (LXIII):[87,127]



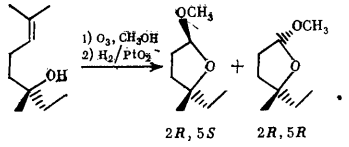
Glyoxylic acid has been used as the reductant in acetic acid[238]. Triphenylphosphine has been employed for the reduction of ozonides[239–241]. Thus the ozonides of substituted methyleneadamantantanes were converted quantitatively into adamananone after being refluxed with triphenylphosphine in hexane for 2 h.[83] The reduction of the ozonides of substituted cyclopentenes led to cyclic triacetals with the adamantane structure[26]:



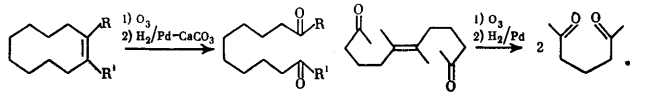
The ozonide of hexakis(trifluoromethyl)benzvalene has been reduced with an equimolar amount of triphenylphosphine to the diketone (LXV), which underwent further transformations in the presence of an excess of the reagent[242]:



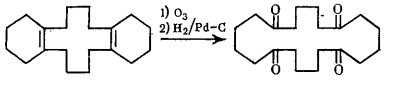
Methoxyhydroperoxides have been reduced electrolytically to aldehydes[243]. Selective hydrogenation on platinum group metals is a modern method[1,16,34,244–246]. Under these conditions, the product of the ozonolysis of dihydrolinalol in methanol gives rise to enantiomeric cyclic acetals, which have been separated by preparative gas–liquid chromatography[247]:



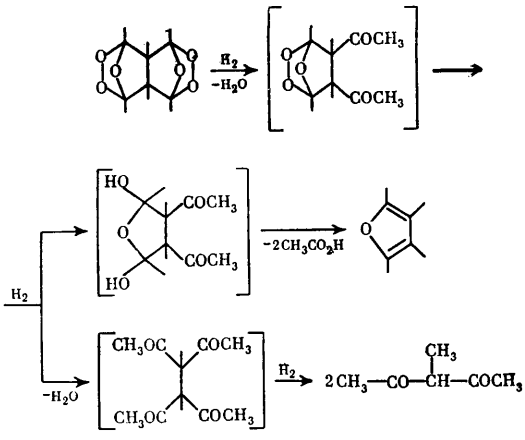
The hydrogenation of ozonides yields mainly the corresponding aldehydes, but the formation of carboxylic acids (up to 18%) as a consequence of disproportionation has also been noted[248]. If cyclohexene is ozonised in the absence of oxygen and then hydrogenated (Pd/C), then 66% of adipic dialdehyde and 24% of 5-formylvaleric acid are obtained[249]. The hydrogenation of the ozonides of substituted methyleneadamantanes results in the formation of adamantanone and the lactone (XLVIII).[83] Diketones have been obtained from cyclic[250] and linear[251] olefins with a substituted double bond:



Reductive ozonolysis has been used to synthesise macrocyclic ketones[149]:

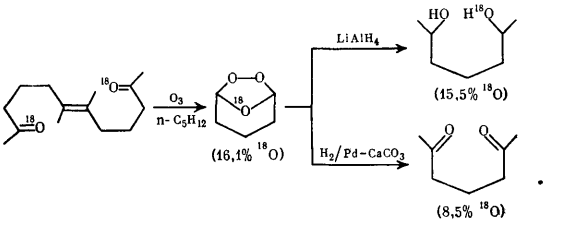


The hydrogenation of the diozonide of Dewar hexamethylbenzene led[106] to tetramethylfuran, which was identified in the form of the adduct with maleic anhydride, and to 3-methylpentane-2,4-dione:

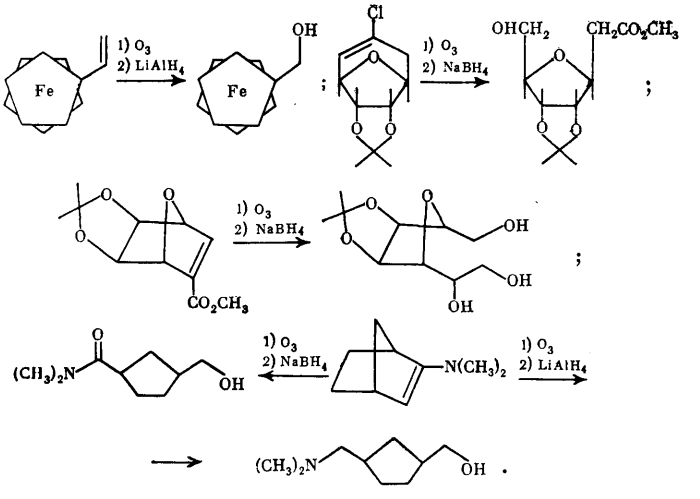


If the catalytic hydrogenation of ozonides is carried out under more severe conditions, the corresponding alcohols and glycols are obtained[252]. In the presence of amines the products are aliphatic amines[253], while diamines have been obtained from the cross-products of the ozonolysis of cycloolefins[254–256].

Complex alkali metal hydrides[1,257], boron[258], and organoaluminium compounds[259] are convenient reagents for the conversion of ozonides into alcohols. The complexes of lithium tetrahydroaluminate with chiral alcohols have reduced ozonides to optically active compounds[260]. The reaction with lithium tetrahydroaluminate takes place quantitatively with selective loss of the oxygen atom from the peroxide bridge, while in the hydrogenation over a palladium catalyst an oxygen atom is split off from both the peroxide and ether bridges[54]:

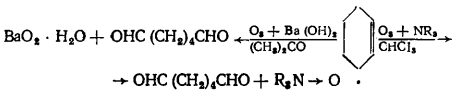


Reductive cleavage with complex alkali metal hydrides has been used in the ozonolysis of olefinic ferrocenes[261] and in the synthesis of intermediates for nucleosides[262] and other physiologically active compounds[263]:

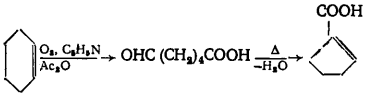


The "non-peroxide" reductive ozonolysis, carried out in the presence of compounds which take up peroxide oxygen, is of practical interest. One of the first versions was ozonolysis in the presence of tetracyanoethylene[65,264,265].

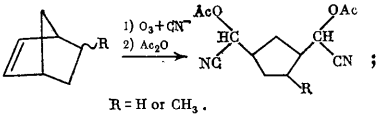
The ability of alkoxyhydroperoxides to epoxidise the double bond has been reported[266]. The reductive ozonolysis of olefins in the presence of "Baeyer–Villiger solvents" (pinacoline, cyclohexanone, and propionaldehyde)[22,23,267] was not confirmed in subsequent studies[24,27,268]. Carbonyl compounds are obtained in a single stage in ozonisation in the presence of pyridine[150], tertiary aliphatic amines[269,290], and alkaline earth metal hydroxides[271,272]:



When cyclohexene is ozonised in the presence of pyridine and acetic anhydride, then, apart from adipic acid (30%), 5-formylvaleric acid is formed (in 35–40% yield) and cyclises at an elevated temperature[273]:



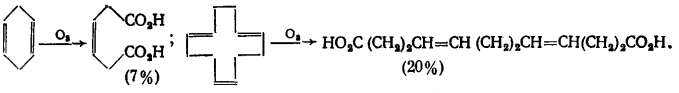
Emulsion ozonisation in the presence of reactive nucleophiles leads to non-peroxide ozonolysis products[35,274–278]. Cyanozonolysis has been applied to bicyclic olefins[279]:



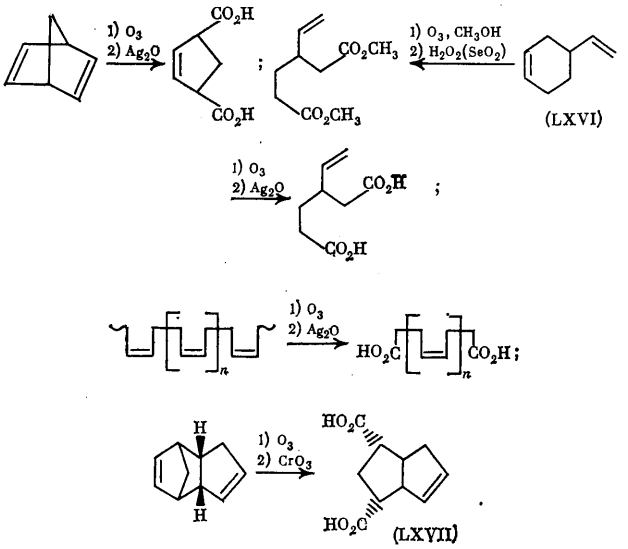
R = H or CH_3.

Methods have been developed for the determination of the positions of the double bonds in alkenes by ozonolysis and oxidation (with silver azide[280]) or reduction (with dimethyl sulphide[40,281] and triphenylphosphine[282]) and subsequent GLC analysis of the methyl esters of carboxylic acids or carbonyl compounds. The oxidative and reductive ozonolytic analytical methods have been compared[283,284]. Oxidative ozonolysis has been applied to natural rubber[285], butyl-rubber[286,287], 3-methylheptatriene–methacrylic acid copolymer[288], a mixture of isomeric bicyclic olefins[289], and natural unsaturated aliphatic acids[290]. The structures of polypiperylene[291] and isobutene oligomers[292] have been established by the ozonolysis of olefins in ethereal solvents. Reductive ozonolysis has been used to determine the structures of rubbers[293–297], poly(vinyl chloride)[298–300] and other polymers[301–303], oligomers[304], cellulose[305], and aliphatic acids[306]. The optical purities of *cis*- and *trans*-olefins have been determined with its aid[307].

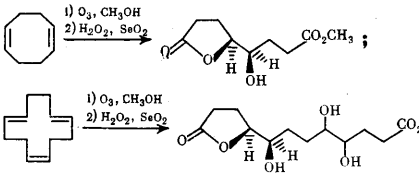
Recently increasing attention has been devoted to the problem of the selectivity of chemical reactions[308,309]. In relation to the ozonolysis reaction, this problem has acquired particular importance for the specific cleavage of one of the multiple bonds in polyunsaturated compounds. Until recently, such compounds have been subjected merely to complete ozonisation in order to establish their structures. It was assumed that partial ozonolysis can be successfully achieved only when the double bonds are conjugated, whereupon the ozonide group formed exerts a significant influence on the remaining double bond, as, for example, in cyclohexa-1,3-diene[310] and p-divinylbenzene[11]. If the double bonds were separated by one or two carbon atoms, the unsaturated dicarboxylic acid could be obtained only in a low yield[310]:



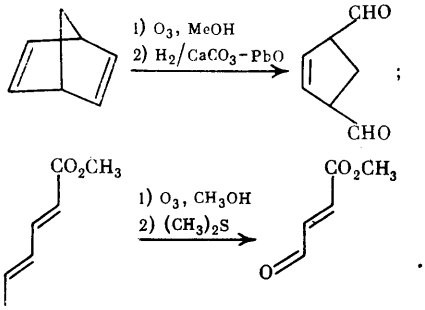
The yields of unsaturated α,ω-dicarboxylic acids increase to 50–60% in emulsion ozonisation in aqueous alkaline hydrogen peroxide[311,312]. The Asinger oxidation of the peroxy-products of the controlled ozonolysis of norbornadiene[313], 4-vinylcyclohexene (LXVI), [314–316] and poly-*cis*-buta-1,4-diene[317] led to the synthesis of the corresponding unsaturated dicarboxylic acids. The diester of 3-vinyladipic acid has been obtained by the selenium dioxide-catalysed decomposition of the peroxy-product of the partial ozonolysis of the diene (LXVI) in methanol[193,199]. Treatment of the product of the controlled ozonolysis of *endo*-dicyclopentadiene[318] with Jones' reagent yielded the acid (LXVII):



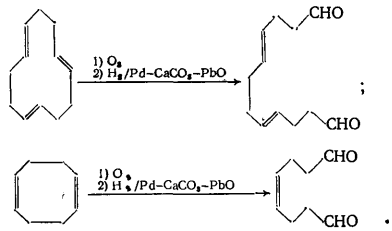
When hydrogen peroxide is used for the decomposition of the ozonides of polybutadiene[205,319,320] and polyisoprene[205,320], the hydroxylation of the double bonds results in the formation of the γ- and δ-lactones[205]. It has been shown in relation to the partial ozonolysis of the cyclic oligomers of 1,3-dienes[321,322] that this reaction is stereospecific in the presence of selenium dioxide[323]:



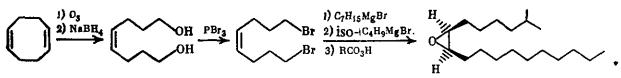
Considerable synthetic possibilities are inherent in partial reductive ozonolysis[313,324–326]:



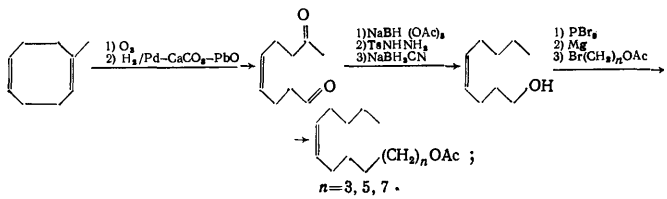
The synthesis of substances regulating the populations of insects[327-332] requires unsaturated aldehydes and ketone with a specific configuration. As a result of the selective ozonolysis of cyclic oligomers of 1,3-dienes[333], such carbonyl compounds have become available:



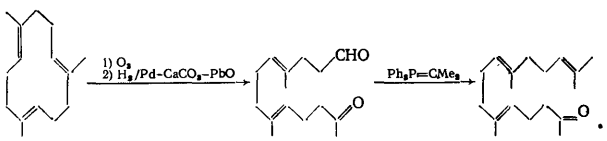
The synthesis of disparlure—the sexual attractant of the silkworm moth—has been developed on the basis of the product of selective ozonolysis of *cis,cis*-cyclo-octa-1,5-diene[334,335]:



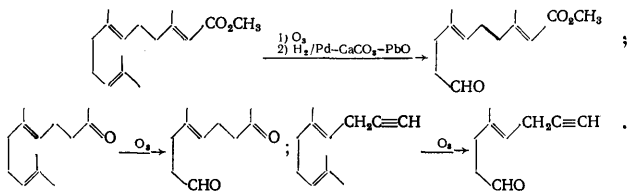
The selective cleavage of the trisubstituted double bond in 1-methyl-*cis,cis*-cyclo-octa-1,5-diene[336] constituted the basis of a new approach to the synthesis of the sexual attractants of coleoptera. These compounds have the structure of *cis*-enol acetates[330,331]:



A new stereospecific synthesis of terpenoid 1,5-polyenes involves the selective ozonolysis of cyclic isoprene oligomers[337,338]:

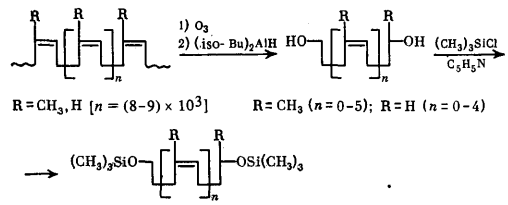


The selective ozonolysis of the isopropylidene group in linear isoprenoid compounds[339] constitutes a convenient method of synthesising regular isoprenoid blocks with terminal functional groups and double bonds having a specified configuration, which are necessary for the construction of polypropenols[340,341]:

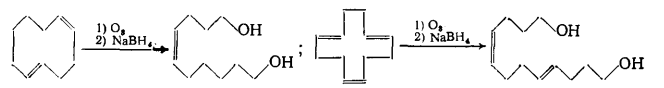


Oligomeric blocks with terminal hydroxy-groups, which have found applications as monomers, plasticisers, adhesives, coatings, and binders for rocket fuel[348], are obtained by the controlled ozonolysis of *cis*-1,4-polybutadiene[259,342,343], *cis*-1,4-polyisoprene[344,345], and copolymers of 1,3-dienes[346,347] with subsequent reduction of the ozonides.

A new approach to the synthesis of bifunctional *cis*-1,5-polyprenols[349] (from natural rubber or its synthetic analogues) and *cis*-1,5-polyenes[350] (from SKD-*cis*-1,4-polybutadiene rubber) has been developed on the basis of the selective ozonolysis of polyunsaturated rubbers with a regular structure. Individual polyenes have been isolated in the form of bis(trimethylsilyl) ethers:



When the cyclic hydrocarbon contains several double bonds of different geometry, the transoid bond is attacked preferentially[351]:



* *
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Thus the advances achieved in the last decade have led to the inclusion of ozonolysis among the modern methods in the chemistry of olefins. There are considerable prospects for the selective ozonolysis of cyclic and linear oligomers and co-oligomers of 1,3-dienes, which have become extremely readily available in recent years as a result of the vigorous development of the chemistry of metal complex catalysis.

REFERENCES

1. Yu.N.Yur'ev, "Ispol'zovanie Ozona v Organicheskom Sinteze" (The Use of Ozone in Organic Synthesis), Izd.VINIITNeftekhim, Moscow, 1979, 49 pp.
2. R.Criegee, Rec.Chem.Prog., 1957, **18**, 111.
3. R.Huisgen, Angew.Chem., Int.Ed.Engl., 1963, **2**, 633.
4. T.Vrbaski and R.J.Cvetanovic, Canad.J.Chem., 1960, **38**, 1053.
5. D.G.Williamson and R.J.Cvetanovic, J.Amer.Chem. Soc., 1968, **90**, 4248.
6. J.Carles and S.Fliszar, Adv.Chem.Ser., 1972, No.112, 35.
7. P.S.Bailey, J.W.Ward, T.P.Carter, E.Nieh, C.M.Fischer, and A.Y.Khashad, J.Amer.Chem.Soc., 1974, **96**, 6136.
8. P.S.Bailey, J.W.Ward, R.E.Hornish, and F.E.Potts, Adv.Chem.Ser., 1972, No.112, 1.
9. L.A.Hull, I.C.Hisatsune, and J.Heicklen, J.Amer.Chem. Soc., 1972, **94**, 4856.
10. W.G.Alcock and B.Mile, Chem.Comm., 1976, 5.
11. S.D.Razumovskii and G.E.Zaikov, "Ozon i Ego Reaktsii s Organicheskimi Soedineniyami" (Ozone and Its Reactions with Organic Compounds), Izd.Nauka, Moscow, 1974, 322 pp.
12. P.S.Bailey, T.M.Ferrell, A.Rustaiyan, S.Seyhan, and L.E.Unruh, J.Amer.Chem.Soc., 1978, **100**, 894.
13. L.J.Durham and F.L.Greenwood, J.Org.Chem., 1968, **33**, 1629.

14. R.A.Rouse, J.Amer.Chem.Soc., 1974, **96**, 5095.
15. R.P.Lattimer, R.L.Kuczkowski, and C.W.Gillies, J.Amer.Chem.Soc., 1974, **96**, 348.
16. P.S.Bailey, Chem.Rev., 1958, **58**, 925.
17. P.S.Bailey, J.W.Ward, and R.E.Hornish, J.Amer. Chem.Soc., 1971, **93**, 3552.
18. R.W.Murray, Acc.Chem., Res., 1968, **1**, 313.
19. P.G.Gassman and X.Creary, Tetrahedron Letters, 1972, 4411.
20. J.K.Crandall and W.W.Conover, Chem.Comm., 1973, 340.
21. P.R.Story, J.A.Alford, W.C.Ray, and J.R.Burgess, J.Amer.Chem.Soc., 1971, **93**, 3044.
22. P.R.Story, J.A.Alford, J.R.Burgess, and W.C.Ray, J.Amer.Chem.Soc., 1971, **93**, 3042.
23. P.R.Story, E.A.Whited, and J.A.Alford, J.Amer. Chem.Soc., 1972, **94**, 2143.
24. P.S.Bailey, T.P.Carter, C.M.Fischer, and J.A.Thompson, Canad.J.Chem., 1973, **51**, 1278.
25. D.R.Kerur and D.G.M.Diaper, Canad.J.Chem., 1973, **51**, 3110.
26. R.Criegee, A.Banciu, and M.Keul, Chem.Ber., 1975, **108**, 1642.
27. K.R.Kopecky, J.E.Filby, C.Mumford, P.A.Lockwood, and J.Y.Ding, Canad.J.Chem., 1975, **53**, 1103.
28. D.R.Kerur and D.G.M.Diaper, Canad.J.Chem., 1977, **55**, 588.
29. P.S.Bailey, J.A.Thompson, and B.A.Shoulders, J.Amer.Chem.Soc., 1966, **88**, 4098.
30. J.Renard and S.Fliszar, J.Amer.Chem.Soc., 1970, **92**, 2628.
31. P.C.Hiberty, J.Amer.Chem.Soc., 1976, **98**, 6088.
32. R.Criegee, Chem.Z., 1973, **7**, 75.
33. R.Criegee, Annalen, 1953, **583**, 1.
34. A.T.Menyailo and M.V.Pospelov, Uspekhi Khim., 1967, **36**, 662 [Russ.Chem.Rev., 1967(4)].
35. C.Bischoff and Z.Rieche, Z.Chem., 1965, **5**, 97.
36. S.Fliszar and M.Granger, J.Amer.Chem.Soc., 1970, **92**, 3361.
37. S.Fliszar, J.Renard, and D.Simon, J.Amer.Chem. Soc., 1971, **93**, 6953.
38. W.P.Keaveney and J.J.Pappas, Tetrahedron Letters, 1969, 841.
39. S.Fliszar and M.Granger, J.Amer.Chem.Soc., 1969, **91**, 3330.
40. M.M.Smits and D.Hoefman, Anal.Chem., 1972, **44**, 1688.
41. S.Fliszar and J.B.Chylinska, Canad.J.Chem., 1967, **45**, 29.
42. S.Fliszar and J.Carles, J.Amer.Chem.Soc., 1969, **91**, 2637.
43. P.R.Story, R.W.Murray, and R.D.Youssefyeh, J.Amer.Chem.Soc., 1966, **88**, 3144.
44. R.W.Murray, R.D.Youssefyeh, and P.R.Story, J.Amer.Chem.Soc., 1967, **89**, 2429.
45. P.R.Story, C.E.Bishop, J.R.Burgess, R.W.Murray, and R.D.Youssefyeh, J.Amer.Chem.Soc., 1968, **90**, 1907.
46. P.R.Story, C.E.Bishop, J.R.Burgess, J.B.Olson, R.W.Murray, and R.D.Youssefyeh, Adv.Chem.Ser., 1968, No.77, 46.
47. R.W.Murray and R.Hagen, J.Org.Chem., 1971, **36**, 1103.
48. S.Fliszar, J.Carles, and J.Renard, J.Amer.Chem. Soc., 1968, **90**, 1364.
49. J.Castonguay, M.Bertrand, J.Carles, S.Fliszar, and Y.Rousseau, Canad.J.Chem., 1969, **47**, 919.
50. C.W.Gillies, R.P.Lattimer, and R.L.Kuczkowski, J.Amer.Chem.Soc., 1974, **96**, 1536.
51. R.P.Lattimer and R.L.Kuczkowski, J.Amer.Chem. Soc., 1974, **96**, 6205.
52. R.W.Murray and R.Hagen, J.Org.Chem., 1971, **36**, 1098.
53. J.Klopman and C.M.Joiner, J.Amer.Chem.Soc., 1975, **97**, 5287.
54. C.E.Bishop and P.R.Story, J.Amer.Chem.Soc., 1968, **90**, 1905.
55. R.W.Murray and A.Suzui, J.Amer.Chem.Soc., 1973, **95**, 3343.
56. D.P.Higley and R.W.Murray, J.Amer.Chem.Soc., 1974, **96**, 3330.
57. M.Schulz and N.Grossmann, J.prakt.Chem., 1976, **318**, 575.
58. D.P.Higley and R.W.Murray, J.Amer.Chem.Soc., 1976, **98**, 4526.
59. J.Carles and S.Fliszar, Canad.J.Chem., 1970, **48**, 1309.
60. E.Briner and S.Fliszar, Helv.Chim.Acta, 1959, **42**, 1310.
61. R.Youssefueh and P.R.Story, J.Amer.Chem.Soc., 1966, **88**, 3143.
62. F.L.Greenwood, J.Amer.Chem.Soc., 1966, **88**, 3146.
63. L.D.Loan, R.W.Murray, and P.R.Story, J.Amer. Chem.Soc., 1965, **87**, 737.
64. R.Criegee and H.Korber, Chem.Ber., 1971, **104**, 1807.
65. R.Criegee and H.Korber, Adv.Chem.Ser., 1972, No.112, 22.
66. N.L.Bauld, J.A.Thompson, C.E.Hudson, and P.S.Bailey, J.Amer.Chem.Soc., 1968, **90**, 1822.
67. R.Criegee, in "Peroxide Reaction Mechanisms" (Edited by J.O.Edwards), Intersci., New York, 1962, p.29.
68. P.S.Bailey, T.M.Ferrell, A.Rustaiyan, S.Seyhan, and L.E.Unruh, J.Amer.Chem.Soc., 1978, **100**, 894.
69. N.M.Emanuel', G.E.Zaikov, and Z.K.Maizus, "Rol' Sredy v Radikal'no-Tsepnykh Reaktsiyakh Okisleniya Organicheskikh Soedinenii" (The Role of the Medium in the Radical-Chain Oxidation Reactions of Organic Compounds), Izd.Nauka, Moscow, 1973, 279 pp.
70. S.Fliszar and J.Carles, Canad.J.Chem., 1969, **47**, 3921.
71. V.Ramachandran and R.W.Murray, J.Amer.Chem. Soc., 1978, **100**, 2197.
72. S.D.Razumovskii and Yu.N.Yur'ev, Neftekhimiya, 1966, **6**, 737.
73. M.V.Pospelov, A.T.Menyailo, A.T.Bortyan, Yu.A.Ustynyuk, and V.S.Petrosyan, Zhur.Org. Khim., 1973, **9**, 311.
74. E.S.Zelikman, Yu.N.Yur'ev, L.V.Berezova, and V.K.Tsyskovskii, Zhur.Org.Khim., 1971, **7**, 633.
75. M.V.Pospelov, A.T.Menyailo, O.R.Kaliko, T.A.Bortyan, E.S.Belyaev, and Yu.Z.Karasev, Zhur.Org.Khim., 1978, **14**, 247.
76. E.Z.Zelikman, A.A.Syrov, and Yu.N.Yur'ev, Zhur. Org.Khim., 1971, **7**, 1135.
77. A.Rieche, M.Schulz, and D.Becker, Chem.Ber., 1965, **98**, 3627.
78. F.L.Greenwood and H.Rubinstein, J.Org.Chem., 1967, **32**, 3369.
79. I.E.Pokrovskaya, A.T.Menyailo, and A.K.Yakovleva, Neftekhimiya, 1969, **9**, 264.
80. J.E.Tranz, W.S.Knowles, and C.Osuch, J.Org.Chem., 1965, **30**, 4328.
81. A.A.Syrov, E.S.Zelikman, and T.L.Yufa, Neftekhimiya, 1971, **11**, 739.
82. O.V.Topalova and L.A.Shabrova, Symposium, "Osnovnoi Organicheskii Sintez i Neftekhimiya" (Fundamental Organic Synthesis and Petrochemistry), Yaroslavl, 1975, No.4, p.66.

83. M.Keul, Chem.Ber., 1975, **108**, 1198.
84. E.J.Dufek and J.C.Cowan, J.Amer.Oil Chem.Soc., 1970, **47**, 51.
85. P.H.Perry, J.Org.Chem., 1959, **24**, 829.
86. V.N.Odinokov, O.S,Kukovinets, and G.A.Tolstikov, Zhur.Org.Khim., 1977, **13**, 2342.
87. V.N.Odinokov, O.S.Kukovinets, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 81.
88. V.N.Odinokov, L.P.Zhemaiduk, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 54.
89. K.Griesbaum and J.Brüggemann, J.Adv.Chem.Ser., 1972, No.112, 50.
90. R.C.Slagel, J.Org.Chem., 1966, **31**, 593.
91. R.Criegee and R.Noll, Annalen, 1959, **627**, 1
92. J.C.Robertson and W.J.Verzino, J.Org.Chem., 1970, **35**, 545.
93. D.G.Diaper, Canad.J.Chem., 1968, **46**, 3095.
94. S.D.Razumovskii, G.A.Niazashvili, I.A.Tautorskii, and Yu.N.Yur'ev, Vysokomol.Soed., 1971, **13A**, 190.
95. I.E.Pokrovskaya, A.T.Menyailo, and A.K.Yakovleva, in "Uspekhi Khimii Organicheskikh Perekisnykh Soedinenii i Autookisleniya" (Advances in the Chemistry of Organic Peroxy-Compounds and Autoxidation) (Edited by N.N.Emanuel'), Izd.Khimiya, Moscow, 1969, p.124.
96. R.Criegee, Chimia, 1968, **22**, 385.
97. R.Criegee and R.Rucktäschel, Chem.Ber., 1970, **103**, 50.
98. R.Criegee and R.Huber, Chem.Ber., 1970, **103**, 1862.
99. H.Christl and G.Brüntup, Chem.Ber., 1974, **107**, 3908.
100. Y.Kobayashi, I.Kumadaki, A.Ohsawa, J.Hanzawa, M.Honda, and Y.Iitaka, Tetrahedron Letters, 1975, 3001.
101. V.R.Skvorchenko, I.E.Pokrovskaya, A.G.Shil'nikova, and R.Ya.Levina, Zhur.Org.Khim., 1969, **5**, 1998.
102. S.Gäb, S.Nitz, H.Parlar, and F.Korte, Angew. Chem., 1976, **88**, 479.
103. C.W.Gillies, J.Amer.Chem.Soc., 1977, **99**, 7239.
104. R.P.Lattimer, U.Mazur, and A.Kuczkowski, J.Amer. Chem.Soc., 1976, **98**, 4012.
105. R.Criegee and H.Korber, Annalen, 1972, **756**, 95.
106. H.N.Junker, W.Schäfer, and H.Niedenbrück, Chem. Ber., 1967, **100**, 2508.
107. R.Criegee, G.Schröder, G.Maier, and H.G.Fischer, Chem.Ber., 1960, **93**, 1553.
108. R.W.Murray, P.R.Story, and L.D.Loan, J.Amer. Chem.Soc., 1965, **87**, 3025.
109. R.Criegee and H.Korber, Chem.Ber., 1971, **104**, 1812.
110. M.Schultz and K.Kirschke, Adv.Heterocycl.Chem., 1967, No.8, 165.
111. K.Griesbaum, Chem.Ber., 1968, **101**, 463.
112. R.Criegee, Chem.Ber., 1975, **108**, 743.
113. R.Criegee and A.Rustaiyan, Chem.Ber., 1975, **108**, 749.
114. M.Keul, Chem.Ber., 1975, **108**, 1207.
115. I.J.Borowitz and R.D.Rapp, J.Org.Chem., 1969, **34**, 1370.
116. P.R.Story and J.R.Burgess, J.Amer.Chem.Soc., 1967, **89**, 5726.
117. R.E.Erickson and G.D.Mercer, Adv.Chem.Ser., 1972, No.112, 114.
118. P.R.Story and J.R.Burgess, Tetrahedron Letters, 1968, 1287.
119. P.Kolsaker and P.S.Bailey, Acta Chem.Scand., 1967, 21, 537.
120. A.Rieche, Angew Chem., 1958, **70**, 251.
121. R.W.Murray, J.W.P.Lin, and D.A.Crumke, Adv. Chem.Ser., 1972, No.112, 9.
122. G.L.Lange and E.Neidert, J.Org.Chem., 1975, **40**, 3604.
123. K.H.Overton and P.Owen, J.Chem.Soc., Perkin Trans.I, 1973, 226.
124. K.Griesbaum and J.Brüggemann, Chem.Ber., 1972, **105**, 3638.
125. K.Griesbaum and P.Hoffmann, J.Amer.Chem.Soc., 1976, **98**, 2877.
126. S.D.Razumovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 335.
127. V.N.Odinokov, O.S.Kukovinets, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 1209.
128. R.M.Ellam and J.M.Padbury, Chem.Comm., 1971, 1094.
129. D.R.Kerur and D.G.M.Diaper, Canad.J.Chem., 1972, **50**, 4029.
130. E.Bernatek, H.Hagen, and T.Ledaal, Acta Chem. Scand., 1967, **21**, 1555.
131. O.V.Topalova, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No.2990-75 Dep.); Ref.Zhur.Khim., 1976, 15Zh174.
132. E.S.Zelikman, L.V.Berezova, Yu.N.Yur'ev, and E.P.Tarasenkov, Zhur.Org.Khim., 1973, **9**, 1140.
133. French Appl.2309506 (1975); Ref.Zhur.Khim., 1977, 24N68.
134. USSR P.556135 (1975); Byul.Izobret., 1977, No.16, 65.
135. V.N.Odinkov, L.P.Zhemaiduk, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1900.
136. Ya.G.Mukhtarov, V.N.Odinokov, G.Yu.Ishmuratov, and G.A.Tolstikov, Neftekhimiya, 1978, **18**, 30.
137. C.Nebel, Chem.Comm., 1968, 101.
138. K.Griesbaum and H.Keul, Angew.Chem., 1975, **87**, 748.
139. A.H.Andrist and M.J.Kovelan, J.Chem.Soc., Perkin Trans.I, 1978, 918.
140. G.Nagendrapps and K.Griesbaum, J.Agr.Food Chem., 1978, **26**, 581.
141. D.R.Kerur and D.G.M.Diaper, Canad.J.Chem., 1969, **47**, 43.
142. W.Adam, Angew.Chem., 1974, **86**, 683.
143. F.R.Wight, Tetrahedron Letters, 1976, 3691.
144. G.Ohloff, Pure Appl.Chem., 1975, **43**, 481.
145. R.W.Murray, W.C.Lumma, and J.W.Lin, J.Amer. Chem.Soc., 1970, **92**, 3205.
146. A.P.Schaap and P.D.Barlett, J.Amer.Chem.Soc., 1970, **92**, 6055.
147. F.E.Stary, D.E.Emgl, and R.W.Murray, J.Amer. Chem.Soc., 1976, **98**, 1880.
148. P.R.Story and P.Busch, Adv.Org.Chem., 1972, No.8, 67.
149. B.Lee, P.R.Story, and J.R.Sanderson, J.Org.Chem., 1976, **41**, 2314.
150. K.Griesbaum, Brennstoff-Chemie, 1969, **50**, 212.
151. R.W.Murray, in "Ozone Chemistry and Technology" (Edited by J.S.Murphy and J.R.Orr), Franklin Inst. Press, Philadelphia, 1975, p.85.
152. A.Takamizawa, S.Matsumoto, T.Iwata, and I.Makino, Chem.Pharm.Bull., 1977, **25**, 1877.
153. A.T.Menyailo, A.K.Ryzhankova, and I.E.Pokrovskaya, Neftepererabotka i Neftekhimiya, 1975, No.7, 35.
154. K.D.Carlson, V.E.Sohns, R.B.Perkins, and E.L.Huffman, Ind.Eng., Chem.Prod.Res.and Devlop. 1976, **16**, 95.

155. USSR P.502869 (1972); Byul.Izobret., 1976, No.6, 50.
156. USSR P.390066 (1970); Byul Izobret., 1973, No.30, 72.
157. US P.3676473 (1969).
158. US P.3676489 (1969).
159. Japanese P.48-40346 (1969); Ref.Zhur.Khim., 1974, 16N83.
160. USSR P.433126 (1972); Byul.Izobret., 1974, No.23, 59.
161. Japanese P.48-21928 (1970); Ref.Zhur.Khim., 1974, 10N61.
162. BRD P.1183065 (1963); Chem.Abs., 1965, **62**, 10378.
163. A.S.Narula and S.Dev, Tetrahedron Letters, 1969, 1733.
164. USSR P.592814 (1976); Byul.Izobret., 1978, No.6, 99.
165. D.T.C.Yang, Org.Prep. and Proced.Int., 1976, **8**, 237.
166. J.K.Stille and J.L.Eichemlberger, J.Org.Chem., 1970, **36**, 1840.
167. E.J.Dufen, J.C.Cowan, and J.P.Friedrich, J.Amer. Oil.Chem.Soc., 1970, **47**, 51.
168. I.E.Pokrovskaya, A.K.Ryzhankova, A.T.Menyailo, T.I.Semenova, and Yu.Z.Karasev, Neftekhimiya, 1972, **12**, 98.
169. S.D.Razumovskii and G.E.Zaikov, Zhur.Org.Khim., 1972, **8**, 464.
170. G.N.Freidlin, "Alifaticheskie Dikarbonovye Kisloty" (Aliphatic Dicarboxylic Acids), Izd.Khimiya, Moscow, 1979, 263 pp.
171. O.S.Shchetinskaya, S.M.Sedova, G.L.Vesel'chakova, and A.M.Gol'dman, Khim.Prom., 1976, 486.
172. USSR P.497282 (1973); Byul.Izobret., 1975, No.48, 74.
173. V.N.Odinokov, R.I.Galeeva, G.A.Tolstikov, L.V.Spirikhin, and E.E.Zaev, Zhur.Org.Khim., 1977, **13**, 1195.
174. J.E.Franz, W.S.Knowles, and C.Osuch, J.Org.Chem., 1965, **30**, 4328.
175. US P.3281429 (1966); Chem.Abs., 1967, **66**, 10582.
176. B.R.Moldavskii and V.G.Bebel', Zhur.Prikl.Khim., 1963, **36**, 1614.
177. USSR P.374277 (1971); Byul.Izobret., 1973, No.15, 45.
178. V.N.Odinokov, R.I.Galeeva, and G.A.Tolstikov, Zhur.Org.Khim., 1973, **9**, 666.
179. USSR P.555087 (1977); Byul.Izobret., 1977, No.15, 67.
180. Japanese P.51-6664 (1970); Ref.Zhur.Khim., 1977, 2043.
181. USSR P.407881 (1972); Byul.Izobret., 1973, No.47, 80.
182. USSR P.380636 (1971); Byul.Izobret., 1973, No.21, 84.
183. D.G.M.Diaper, Canad.J.Chem., 1966, **44**, 2819.
184. B.P.1196598 (1967).
185. Q.E.Thompson, J.Org.Chem., 1962, **27**, 4498.
186. B.P.1196596 (1967).
187. US P.3192233 (1965); Chem.Abs., 1965, **63**, 8482.
188. H.Obara, S.Kumazawa, J.Onodera, and H.Kimura, J.Chem.Soc.Japan, Chem. and Ind.Chem., 1974, 2380.
189. US P.3437667 (1969); Chem.Abs., 1969, 71, 3052.
190. French Appl.7538067 (1977); Ref.Zhur.Khim.. 1978, 21N114.
191. USSR P.445644 (1972); Byul.Izobret., 1974, No.37, 60.
192. V.N.Odinokov, R.I.Galeeva, N.A.Muradova, and G.A.Tolstikov, Neftekhimiya, 1974, **14**, 441.
193. V.N.Odinokov, R.I.Galeeva, N.A.Muradova, and G.A.Tolstikov, Symposium, "Khimiya i Fiziko-Khimiya Monomerov" (The Chemistry and Physical Chemistry of Monomers), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1975, p.72.
194. USSR P.414256 (1972); Byul.Izobret., 1974, No.5, 84.
195. V.N.Odinokov, R.I.Galeeva, and G.A.Tolstikov, Symposium, "Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov" (The Chemistry and Technology of Organoelemental Compounds and Polymers), Kazan, 1972, Nos.1–2, p.62.
196. V.N.Odinokov, R.I.Galeeva, and G.A.Tolstikov, Zhur.Org.Khim., 1973, **9**, 2303.
197. V.Sh.Shaikhrazieva, E.V.Tal'vinskii, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1618.
198. V.Sh.Shaikhrazieva, E.V.Tal'vinskii, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 1522.
199. V.N.Odinokov, L.B.Zhemaiduk, A.I.Odinokova, and G.A.Tolstikov, Neftekhimiya, 1975, **15**, 446.
200. V.N.Odinokov, L.B.Zhemaiduk, A.I.Odinokova, and G.A.Tolstikov, Zhur.Org.Khim., 1977, **13**, 2078.
201. E.P.Baldwin, G.W.Burton, K.Griesbaum, and G.Hunigton, Adv.Chem.Ser., 1969, No.91, 448.
202. French P.1567125 (1966); Chem.Abs., 1969, 71, 125719.
203. US P.3346631 (1962); Chem.Abs., 1967, **67**, 11781.
204. USSR P.466207 (1973); Byul.Izobret., 1975, No.13, 50.
205. V.N.Odinokov, R.G.Timirova, and G.A.Tolstikov, Symposium, "Khimiya i Fiziko-Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry and Physical Chemistry of Macromolecular Compounds), Izd. Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1975, p.165.
206. Japanese P.52-144619 (1977); Ref.Zhur.Khim., 1978, 19H54.
207. L.Long, Chem.Rev., 1940, **27**, 437.
208. O.V.Topalova and L.A.Shabrova, Zhur.Org.Khim., 1975, **11**, 2444.
209. A.T.Menyailo, M.V.Pospelov, O.R.Kaliko, and A.I.Shekuteva, in "Uspekhi Khimii Organicheskikh Perekisnykh Soedinenii i Autookisleniya" (Advances in the Chemistry of Organic Peroxy-Compounds and Autoxidation)(Edited by N.M.Emanuel'), Izd.Khimiya, Moscow, 1969, p.314.
210. I.K.Kochi and P.E.Mocadlo, J.Org.Chem., 1965, **30**, 1134.
211. DDR P.1928705 (1968); Chem.Abs., 1970, **72**, 100070.
212. S.Gäb, S.Nitz, H.Parlar, and F.Korte, Angew.Chem., 1976, **88**, 479.
213. G.L.Lange and T.W.Hall, J.Org.Chem., 1974, **39**, 3819.
214. US P.3565892 (1968); Chem.Abs., 1971, **75**, 36041.
215. E.D.Brown, J.K.Sutherland, and T.W.Sam, J.Chem. Soc., Perkin Trans.I, 1975, 2332.
216. J.Ide, T.Hiraoka, and Y.Kishida, Bull.Chem.Soc. Japan, 1976, **49**, 3243.
217. J.Kulesza, J.Kula, and E.Ulatowska-Wdowiak, Roczniki Chem., 1975, **49**, 1911.
218. E.J.Dufek, J.C.Cowan, and J.P.Friedrich, J.Amer. Oil Chem., 1970, **47**, 51.
219. R.A.Awl and E.H.Pryde, J.Amer.Oil Chem.Soc., 1966, **43**, 35.
220. J.J.Borowitz and D.R.Robert, J.Org.Chem., 1969, **34**, 1370.
221. F.N.Jones and R.V.Lindsey, J.Org.Chem., 1968, **33**, 3838.

222. J.J.Pappas and W.P.Keaveney, Tetrahedron Letters, 1966, 4273.
223. US P.3637721 (1970).
224. Swiss P.514528 (1967).
225. USSR P.521254 (1974); Byul.Izobret., 1976, No.26, 74.
226. USSR P.521255 (1974); Byul.Izobret., 1976, No.26, 75.
227. T.Sato, R.Ito, Y.Hayakawa, and R.Noyori, Tetrahedron Letters, 1978, 1829.
228. L.I.Zakharkin and A.I.L'vov, Zhur.Obshch.Khim., 1967, **37**, 742.
229. E.Logemann and G.Schill, Chem.Ber., 1977, **110**, 3228.
230. E.Logemann, G.Schill, C.Zürcher, and H.Fritz, Chem.Ber., 1978, **111**, 1019.
231. G.Jones, R.A.Raphael, and W.Wright, Chem.Comm., 1972, 609.
232. B.P.1439544 (1973).
233. R.D.Clark and C.H.Heathcock, J.Org.Chem., 1976, **41**, 1396.
234. F.Frickel, Synthesis, 1974, 507.
235. U.Husstedt and H.J.Schafer, J.Chem.Res.Synop., 1977, No.6, 131.
236. USSR P.535280 (1974); Byul.Izobret., 1976, No.42, 56.
237. V.N.Odinokov, O.S.Kukovinets, and G.A.Tolstikov, Zhur.Org.Khim., 1976, **12**, 568.
238. P.Kolsaker, E.Bernatek, R.Johanson, and R.Hytta, Acta Chem.Scand., 1973, **27**, 1526.
239. O.Lorenz and C.R.Parks, J.Org.Chem., 1965, **30**, 1976.
240. O.Lorenz, Anal.Chem., 1965, **37**, 101.
241. H.J.Bestmann, J.Kantardjiew, P.Rösel, W.Stansky, and O.Vostrowsky, Chem.Ber., 1978, **111**, 248.
242. Y.Kobayashi, Y.Hanzawa, and Y.Nakanishi, Tetrahedron Letters, 1977, 3371.
243. US P.3658667 (1970).
244. H.Lettre and D.Hotz, Annalen 1959, **620**, 63.
245. US P.3705922 (1972).
246. Japanese P.19929 (1968); Ref.Zhur.Khim., 1972, 5N45.
247. W.J.Richter, Annalen, 1975, 401.
248. N.G.Gil'chenok, Neftekhimiya, 1975, **15**, 848.
249. G.Hesse and E.Bayer, Z.Naturforsch., 1964, **19B**, 875.
250. K.J.Ploner and P.Heimbach, Annalen, 1976, 54.
251. A.F.Diaz, L.Lardins, and S.Winstein, J.Amer.Chem. Soc., 1968, **90**, 1905.
252. R.W.White, S.W.King, and J.L.O'Brien, Tetrahedron Letters, 1971, 3587.
253. K.A.Pollart and R.E.Miller, J.Org.Chem., 1962, **27**, 2392.
254. R.W.White, S.W.King, and J.L.O'Brien, Tetrahedron Letters, 1971, 3591.
255. French Appl.2328692 (1976); Ref.Zhur.Khim., 1978, 14N89.
256. Japanes P.49-24446 (1970); Ref.Zhur.Khim., 1975, 5N63.
257. A.Hubert, J.Chem.Soc., 1961, 4088.
258. D.G.M.Diaper and W.M.Strachan, Canad.J.Chem., 1967, **45**, 33.
259. USSR P.590314 (1975); Byul.Izobret., 1978, No.4, 91.
260. D.Seebach and H.Daum, Chem.Ber., 1974, **107**, 1748.
261. S.I.Goldberg and W.D.Loeble, J.Org.Chem., 1968, **33**, 2971.
262. W.J.Gensler, S.Chan, and D.B.Ball, J.Amer.Chem. Soc., 1975, **97**, 436.
263. G.Just, A.Martel, K.Grozinger, and M.Ramjeesingh, Canad.J.Chem., 1975, 131.
264. R.Criegee and P.Günther, Chem.Ber., 1963, **96**, 1564.
265. H.Kwart and D.M.Hoffman, J.Org.Chem., 1966, **31**, 419.
266. I.E.Pokrovskaya, I.K.Alferova, and Kh.E.Khcheyan, Neftekhimiya, 1967, **13**, 247.
267. US P.3862142 (1972).
268. N.C.Yang and J.Libman, J.Org.Chem., 1974, **39**, 1782.
269. I.E.Pokrovskaya, A.T.Menyailo, A.K.Ryzhankova, and L.S.Mishina, Neftekhimiya, 1971, **11**, 873.
270. USSR P.266761 (1970); Byul.Izobret., 1970, No.12, 24.
271. I.E.Pokrovskaya, A.T.Menyailo, M.V.Pospelov, A.K.Ryzhankova, A.G.Shil'nikova, G.N.Dudnik, and L.S.Mishina, Neftekhimiya, 1970, **10**, 554.
272. V.V.Fedorova, I.E.Pokrovskaya, A.T.Menyailo, and T.F.Narozhenko, Izv.Vys.Shkoly, Khim.i Khim. Tekhnol., 1972, 526.
273. V.N.Odinokov, A.I.Odinokova, and G.A.Tolstikov, Zhur.Org.Khim., 1973, **9**, 671.
274. E.K.Fields, "Proceedings of the VIIth World Petroleum Congress, 1967, Mexico, 1968, Vol.5, p.24.
275. E.K.Fields, "Proceedings of the VIIth World Petroleum Congress, 1967, Mexico, 1968, Vol.5, p.45.
276. US P.3503995 (1966).
277. US P.3503997 (1969).
278. US P.4354641 (1966).
279. V.N.Odinokov, A.I.Odinokova, O.S.Kukovinets, and G.A.Tolstikov, Symposium, "Khimiya i Fiziko-Khimiya Monomerov" (The Chemistry and Physical Chemistry of Monomers), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1975, p.225.
280. T.Lesment and S.Faingold, Izv.Akad.Nauk Est.SSR, Khim.Issled., 1967, **16**, 19.
281. M.J.Hackathorn and M.J.Brook, J.Polymer Sci., 1975, **13**, 945.
282. M.Beroza and B.A.Bierl, Anal.Chem., 1967, **39**, 1131.
283. A.Greiner, J.prakt.Chem.[4], 1965, **27**, 69.
284. J.Hoffman, J.Smidova, and S.Landa, Coll.Czech. Chem.Comm., 1970, **35**, 2174.
285. G.P.McSweeney, J.Polymer Sci., A-1, 1968, **6**, 2678.
286. I.N.Zaripov, V.V.Beresnev, P.A.Kirpichnikov, and L.I.Nikitina, Symposium, "Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov" (The Chemistry and Technology of Organoelemental Compounds and Polymers), Kazan, 1974, p.20.
287. V.I.Gordienko, V.I.Valuev, R.A.Shlyakhter, and G.N.Sinaiskii, Kauchuk i Rezina, 1975, No.1, 4.
288. A.I.Vorob'eva, M.A.Gurevich, G.V.Leplyanin, S.R.Rafikov, R.G.Timirova, and V.N.Odinokov, Vysokomol.Soed., 1974, **16A**, 1826.
289. J.D.Deyrup and M.F.Betkouski, J.Org.Chem., 1975, **40**, 284.
290. E.P.Crowell, S.M.Aronic, and B.B.Burnett, J.Chromatog.Sci., 1971, **9**, 296.
291. A.A.Panasenko, V.N.Odinokov, Yu.B.Monakov, L.M.Khalilov, A.S.Bezgina, V.K.Iganatyuk, and S.R.Rafikov, Vysokomol.Soed., 1957, **19B**, 656.
292. Yu.A.Sangalov, Yu.B.Yasman, V.N.Odinokov, V.K.Ignatyuk, E.M.Il'kaeva, A.G.Svinukhov, and K.S.Minsker, Neftekhimiya, 1977, **17**, 865.
293. A.I.Spasskova and T.S.Sokolova, Vestnik Leningrad. Univ., 1971, No.22, 141.
294. A.I.Spasskova, Vestnik Leningrad.Univ., 1973, No.10, 140.

295. V.S.Shagov, L.P.Andreeva, and A.I.Yakubchik, Vestnik Leningrad.Univ., Ser.Fiz.i Khim., 1973, No.2, 134.
296. V.S.Shagov, A.I.Yakubchik, A.M.Shagulenko, and L.Yu.Lanina, Vysokomol.Soed., 1973, **15A**, 10.
297. V.B.Pebalk, T.I.Poznyak, V.I.Gerbich, and D.M.Lisitsyn, Kauchuk i Rezina, 1972, No.8, 51.
298. A.Michel, G.Schmidt, and A.Guyot, Amer.Chem.Soc. Polym.Prepr., 1973, **14**, 665.
299. W.C.Geddes, Europ.Polymer J., 1967, **3**, 733.
300. K.S.Minsker, A.A.Berlin, D.V.Kazachenko, and R.G.Abdullina, Dokl.Akad.Nauk SSSR, 1972, **223**, 881.
301. R.J.Ambrose and W.L.Hergenrother, Nuovo Cimento, 1973, **49**, 45.
302. M.J.Hackathorn and M.J.Brock, J.Polymer Preprints, Amer.Chem.Soc., Div.Polymer Chem., 1972, **14**, 42.
303. M.Host and D.Deur-Siftar, Chromatographia, 1972, **5**, 502.
304. Z.G.Zemskova, S.D.Razumovskii, N.G.Matveeva, D.M.Lisitsyn, and A.A.Berlin, Vysokomol.Soed., 1972, **14A**, 2263.
305. M.F.Kiryushina and D.V.Tishchenko, Zhur.Prikl. Khim., 1971, **44**, 159.
306. S.Koritala, J.Amer.Oil Chem.Soc., 1973, **50**, 110.
307. A.M.Caporusso, G.Giacomelli, and L.Lardicci, Gazzetta, 1976, **106**, 879.
308. N.M.Emanuel', Uspekhi Khim., 1978, **47**, 1329 [Russ. Chem.Rev., 1978(8)].
309. G.A.Tolstikov, "Reaktsii Gidroperekisnogo Okisleniya" (Hydroperoxide Oxidation Reactions), Izd.Nauka, Moscow, 1976, 200 pp.
310. I.E.Pokrovskaya, A.T.Menyailo, and A.K.Yakovleva, in "Uspekhi Khimii Organicheskikh Perekisnykh Soedinenii i Autookisleniya" (Advances in the Chemistry of Organic Peroxy-Compounds and Autoxidation) (Edited by N.M.Emanuel'), Izd.Khimiya, Moscow, 1969, p.124.
311. M.I.Fremery and E.K.Fields, J.Org.Chem., 1963, **28**, 2537.
312. US P.3284492 (1962); Chem.Abs., 1967, **66**, 28397.
313. C.A.Grob and H.R.Pfaendler, Helv.Chim.Acta, 1970, **53**, 2156.
314. R.H.Perry, Amer.Chem.Soc.Div.Petrol.Chem., Preprints, 1960, **5**, 65.
315. French P.1315332 (1961); Chem.Abs., 1963, **59**, 11263.
316. B.P.945428 (1961); Chem.Abs., 1964, **60**, 10459.
317. Japanese P.44356 (1969); Ref.Zhur.Khim., 1973, 17S281.
318. D.Brewster, M.Myers, J.Ormerod, P.Otter, A.C.B.Smith, M.E.Spinner, and S.Turner, J.Chem. Soc., Perkin Trans.I, 1973, 2796.
319. V.S.Shagov, L.P.Andreeva, and A.I.Yakubchik, Vestnik Leningrad.Univ., 1973, No.10, 134.
320. USSR P.498285 (1975); Byul.Izobret., 1976, No.1, 80.
321. USSR P.550388 (1975); Byul.Izobret., 1977, No.10, 61.
322. USSR P.555088 (1975); Byul.Izobret., 1977, No.15, 67.
323. V.M.Odinokov, L.P.Zhemaiduk, G.Yu.Ishmuratov, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 1617.
324. P.L.Stotter and J.B.Eppner, Tetrahedron Letters, 1973, 2417.
325. Swiss P.514528 (1971).
326. E.J.Corey, J.A.Katzenellenbogen, N.M.Gilman, S.A.Roman, and B.W.Erickson, J.Amer.Chem.Soc., 1968, **90**, 5618.
327. M.Z.Krimer and A.A.Shamshurin, "Khimiya Yuvenil'nogo Gormona i Ego Analogov" (The Chemistry of the Juvenile Hormone and Its Analogue), Izd. Shtiintsa, Kishinev, 1972, 112 pp.
328. Yu.S.Tsizin and A.A.Drabkina, Uspekhi Khim., 1970, **39**, 1074 [Russ.Chem.Rev., 1970(6)].
329. K.V.Lebedeva and T.K.Yudovskaya, Zhur.Vses. Khim.Obshch. im. Mendeleeva, 1973, **18**, 518.
330. M.Jacobson, "Insect Sex Pheromones" (Translated into Russian), Izd.Mir., Moscow, 1976, 391 pp.
331. C.A.Henrick, Tetrahedron, 1977, **33**, 1845.
332. Yu.A.Kondrat'ev, K.V.Lebedeva, and Yu.B.Pyatnova Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1978, **2**. 179.
333. V.N.Odinokov, V.R.Akhunova, R.S.Bakeeva, R.I.Galeeva, A.V.Semenovskii, A.M.Moiseenkov, and G.A.Tolstikov, Zhur.Org.Khim., 1977, **13**, 532.
334. G.A.Tolstikov, V.N.Odinokov, R.I.Haleeva, and R.S.Bakeeva, Tetrahedron Letters, 1978, 1857.
335. G.A.Tolstikov, V.N.Odinokov, R.I.Galeeva, R.S.Bakeeva, and S.R.Rafikov, Dokl.Akad.Nauk SSSR, 1978, **239**, 1377.
336. V.N.Odinokov, G.A.Tolstikov, R.S.Bakeeva, and R.I.Galeeva, "The XIth International Symposium on the Chemistry of Natural Products, Golden Sands, Bulgaria, 1978", p.86.
337. V.N.Odinokov, W.R.Achunova, R.I.Haleeva, U.M.Djemilev, H.A.Tolstikov, A.M.Moiseenkov, and A.V.Semenovsky, Tetrahedron Letters, 1977, 657.
338. G.A.Tolstikov, V.N.Odinokov, V.R.Akhunova, R.I.Galeeva, U.M.Dzhemelev, A.M.Moiseenkov, and A.V.Semenovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 887.
339. V.N.Odinokov, V.R.Akhunova, G.A.Tolstikov, A.V.Semenovskii, and V.L.Mizyuk, Zhur.Org.Khim., 1978, **14**, 1851.
340. V.N.Shibaev, Uspekhi Biol.Khim., 1976, **17**, 187.
341. H.O.Huisman, Pure Appl.Chem., 1977, **49**, 1307.
342. W.D.Stephens, C.R.McIntosh, and C.O.Taylor, Polymer Sci., A-1, 1968, **6**, 1037.
343. French P.1497289 (1967); Chem.Abs., 1968, **69**, 28289.
344. USSR P.480724 (1974); Byul.Izobret., 1975, No.30, 76.
345. V.N.Odinokov, V.K.Ignatyuk, G.A.Tolstikov, Yu.B.Monakov, A.A.Berg, A.M.Shakirova, S.R.Rafikov, and A.A.Berlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1552.
346. J.P.Dole-Robbe, Bull.Soc.chim.France, 1967, 1078.
347. R.A.Rhein and J.D.Indham, Amer.Chem.Soc. Polymer Prepr., 1974, **15**, 60.
348. R.A.Bratanova and L.S.Kurovskaya, Promyshlennost' Sinteticheskogo Kauchuka, 1973, No.6, 21.
349. G.A.Tolstikov, V.N.Odinokov, V.K.Ignatyuk, A.V.Semenovskii, and A.M.Moiseenkov, Dokl.Akad. Nauk SSSR, 1977, **236**, 901.
350. V.N.Odinokov, V.K.Ignatyuk, and G.A.Tolstikov, "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii. Tezisy Kratkikh Soobshchenii" (International Symposium on Macromolecular Chemistry. Abstracts of Brief Communications), Izd.Nauka, Moscow, 1978, Vol.4, p68.
351. V.N.Odinokov, R.S.Bakeeva, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2836.

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