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Dioxiranes: from oxidative transformations to chemiluminescence

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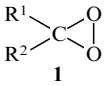
Contents

I.	Introduction	253
II.	Synthesis and spectral characteristics of dioxiranes	254
III.	Thermal decomposition of dioxiranes	257
IV.	Dioxiranes as oxidants	262
V.	Chemluminescence and photochemistry of dioxiranes	274
VI.	Conclusion	280

Abstract. Experimental data on the chemistry of a new class of highly effective oxidation reagents, dioxiranes, are summarised. The main methods used to generate dioxiranes and reactions in which dioxiranes have been proposed as intermediates are considered. The full notion about an important property of dioxiranes, *i.e.* the ability to oxidise rapidly, selectively and under mild conditions various classes of organic compounds (alkanes, alkenes, compounds containing heteroatoms, organometallic substrates, *etc*.) is given. Various aspects and mechanisms of these reactions are discussed. The attention is focused on the analysis of mechanisms of dioxirane decomposition in the absence of oxidisable substrates. One of the most attractive aspects of the dioxirane chemistry, chemiluminescence, is considered (the mechanisms of the generation of excited products during both thermal and catalytic decomposition and upon photochemical activation are discussed). The bibliography includes 401 references.

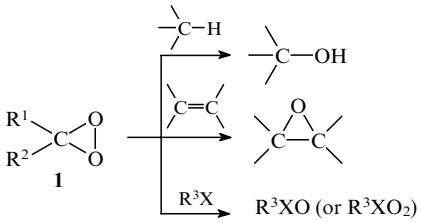
I. Introduction

The chemistry of three-membered cyclic peroxides, dioxiranes **1**, has swiftly developed during the last twelve years.



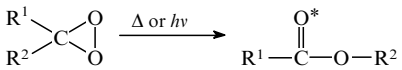
1

In 1985, when successful synthesis of a number of 'isolated alkyldioxiranes'† had been reported,[1] these compounds became available for wide employment. Since then, they have been in the centre of chemists' attention and the number of publications devoted to them has constantly increased. What is the reason for this interest? The main cause is the exceptionally high reactivity of these compounds, which is remarkably combined with high selectivity of oxidation. The most typical reactions of dioxiranes include oxidative functionalisation of alkanes, alkenes and their functionally substituted derivatives containing heteroatoms X



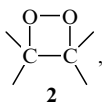
It is this fact that attracts the attention of chemists engaged in organic synthesis to oxiranes. The most often used derivatives are dimethyldioxirane **1a** and methyl(trifluoromethyl)dioxirane **1b**; the oxidative properties of these compounds have been the subject of numerous publications including several excellent reviews,[2–9] devoted mainly to synthetic aspects.

However, this does not exhaust the properties of dioxiranes. Chemiluminescence (CL) is another, equally important feature of these compounds. A fairly attractive feature of dioxiranes, found recently, is that they are capable of forming products in electronically excited states upon both thermal decomposition and photochemical activation.[6,10–17]



(1)

The research along this line started only recently, most of the studies being performed by the authors of this review. Even these few studies allow one to appreciate the great opportunities and prospects opened for researchers in the wonderful world of chemiluminescence of dioxiranes. Although it is difficult to predict the extent to which dioxiranes would be able to compete with their chemical relatives, 1,2-dioxetanes **2** [18–22]



2

† From here on, the term 'isolated dioxirane' implies a solution of dioxirane in the corresponding ketone or in a solvent isolated from the reaction mixture. This term, which is generally accepted in the literature and reflects features of the peroxide method for the synthesis of dioxiranes (see Section II), is used in order to distinguish the cases where isolated dioxiranes are used from those when dioxiranes are generated *in situ* and are not isolated from the reaction mixture.

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it can be claimed with confidence that these three-membered cyclic peroxides have already occupied a special place in the world of shining reactions.

The great interest in dioxiranes is also due to the fact that they represent an isomeric form of carbonyl oxides $R^1R^2C^+ - O - O^-$ (**3**), which are oxidants and important reactive intermediates in many oxidative processes.[23–32] Despite the fact that the behaviours of dioxiranes and carbonyl oxides are substantially different, both should be taken into account in consideration of the mechanisms of some oxidation processes. Moreover, photocyclisation of carbonyl oxides **3** is the main method used to synthesise dioxiranes **1** in a matrix.[33]

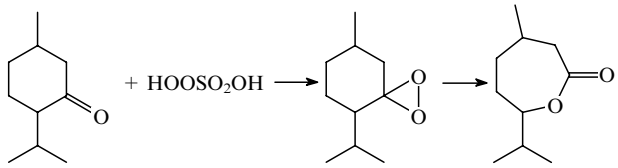
The mechanism of decomposition of dioxiranes in the absence of easily oxidisable partners also presents interest. The mechanism of their reactions with alkanes, which has unexpectedly become the object of sharp debates, is equally interesting (see, for example, Refs 34–39).

There are grounds for believing that dioxiranes can be formed in the upper atmosphere,[1,3,40] upon interaction of alkenes with ozone.[41–44] Study of gas-phase reactions of dioxiranes with polyaromatic hydrocarbons (PAH)[3,45–47] including those yielding carcinogens (which can affect the environment) could provide deeper insight into the processes occurring in the atmosphere.

This review covers these and many other aspects. We hope that it would present interest not only for organic chemists but also for specialists in physical chemistry.

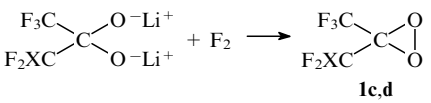
II. Synthesis and spectral characteristics of dioxiranes

The history of the dioxirane chemistry covers almost a century. In 1899, Baeyer and Villiger,[48] who studied the reaction of menthone with monoperoxysulfuric acid, postulated that the formation of the corresponding lactone is preceded by the formation of a cyclic oxygen-containing intermediate, dioxirane.



Now this reaction is named after the authors. They were the first to introduce the term 'dioxirane' into scientific literature. The next mention of dioxiranes dates back to 1910, when Harries[49] suggested that decomposition of 1,2,3-trioxolanes, resulting from ozonisation of alkenes, affords carbonyl oxide and a peroxide and ascribed a dioxirane structure to the latter product.

Only many years after these two publications had appeared, was the first dioxirane really prepared and characterised. This was done by Talbot and Thompson[50] in 1972. The authors reported on the synthesis of perfluorodimethyldioxirane **1c** and chlorodifluoromethyl(trifluoromethyl)dioxirane **1d** by oxidation of the corresponding dialkoxides with fluorine. However, this method has not been further developed.



1c,d

X = F (**c**), Cl (**d**).

The dioxiranes **1c** and **1d** were isolated using low-temperature gas chromatography; they were coloured pale yellow both in the liquid and solid states (the absorption maximum of the dioxirane **1c** lies at $\lambda = 306$ nm).[50] The compound **1c** was described as unstable and explosive.[50]

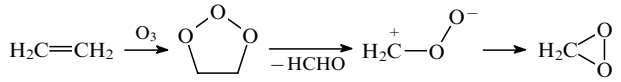
At present, two main lines in the dioxirane synthesis can be distinguished: (1) the peroxide method, which is used most often and successfully to prepare dioxiranes and (2) non-peroxide methods (*e.g.*, ozonolysis of hydrocarbons, photooxidation of diazo compounds in a matrix and some other methods.)

1. Non-peroxide methods for the synthesis of dioxiranes

When considering the known non-peroxide methods for the generation of dioxiranes, we dwelt not only on the studies the authors of which succeeded in isolating dioxiranes and obtaining their spectral characteristics but also on those in which dioxiranes were only suggested as possible intermediates (the latter type is represented by a few examples).

a. Ozonolysis of saturated and unsaturated compounds

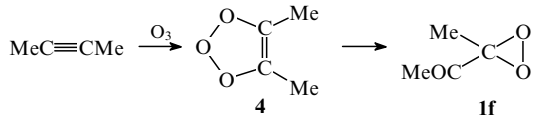
In 1977 two groups of researchers working independently[41–44] presented convincing experimental evidence (obtained by microwave spectroscopy and mass spectrometry) for the formation of the simplest dioxirane **1e** in the gas-phase ozonisation (−130 to −75 °C) of ethylene. Dioxirane **1e** was also detected among the products of ozonolysis of propene, vinyl fluoride and but-1-ene.



1e

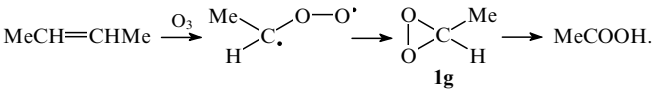
The microwave spectroscopy data showed that dioxirane **1e** has a shorter C–C bond (1.3878 Å) and a longer O–O bond (1.5155 Å) than ethylene ozonide, in which the corresponding bond lengths are 1.416 and 1.461 Å.

A large variety of reactions of ozonisation of unsaturated substrates involving dioxiranes have been reported.[51–59] Thus Keay and Hamilton[51,52] carried out ozonisation of but-2-yne in CH_2Cl_2 (−70 °C). By varying the temperature and adding portions of methanol to the solvent, the researchers isolated three different products, capable of epoxidising alkenes; the first compound was identified as the peroxy acid MeC(O)OOH, the second one was identified as trioxolene **4**, and the structure of dioxirane **1f** was attributed to the third compound.



4 **1f**

Pryor *et al.*[53] carried out a similar reaction in the presence of nitrone as a spin trap; they detected the adduct of the nitrone with the acetyl radical formed from the dioxirane **1f**. Bufalini *et al.*[54] interpreted the formation of acetic acid in the ozonisation of but-2-ene as being due to the following sequence of reactions:

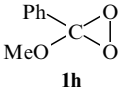


1g

Eastman *et al.*[55,56] explained in a similar way the formation of methyl acetate and an ester of formic acid in the gas-phase ozonisation of tetramethylethylene and cyclohexene.

O'Neal and Blumstein[57] proposed a general mechanism of gas-phase ozololysis based on participation of the biradical form of carbonyl oxide and the subsequent transformation of the biradical into dioxirane. Conversely, Vaccani *et al.*[58] suggested direct formation of dioxirane from 1,2,3-trioxolane during the gas-phase reaction of ozone with vinyl chloride.

The liquid-phase ozonisation of 1,2-dimethoxy-1,2-diphenylethene gave (methoxy)phenyldioxirane **1h**, which was studied by ^{13}C NMR spectroscopy.[59]

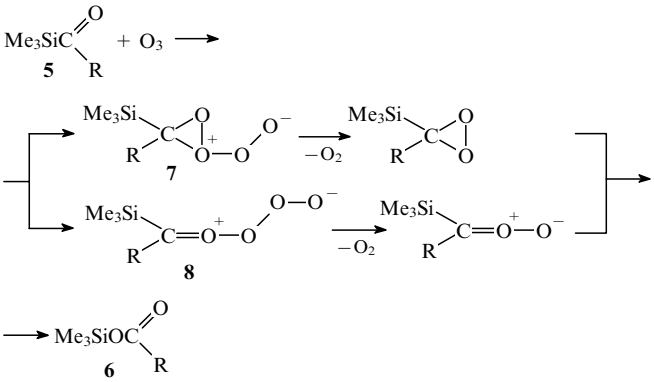


1h

In several studies, dioxiranes have been considered as intermediates in ozonisation of saturated compounds. Thus ozonolysis of ketones **5** occurs presumably[60] *via* an attack by ozone on the

carbonyl group of **5** to give compounds **7** or **8**, which eliminate an oxygen molecule being thus converted into either carbonyl oxide or dioxirane (Scheme 1).

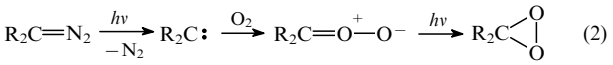
Scheme 1



It has been suggested [61] that the formation of anhydrides in the ozonisation of some α-diketones occurs by a similar scheme.

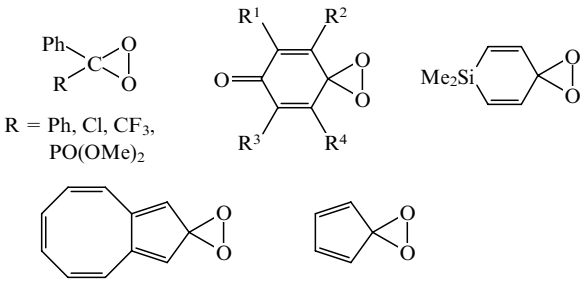
b. Cyclisation of carbonyl oxide to dioxirane in a matrix

Yet another aspect of the dioxirane chemistry is related to low-temperature photochemistry. In a series of studies,[28, 33, 62–72] a new pathway to dioxiranes has been found, which is based on low-temperature irradiation of carbonyl oxides in an argon matrix.

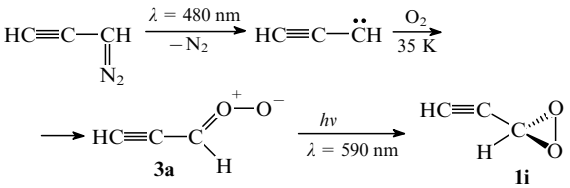


(2)

This method was used to prepare diphenyldioxirane, chloro(phenyl)dioxirane, phenyl(trifluoromethyl)dioxirane, a series of substituted dioxiranes based on quinone *O*-oxides, silicon-containing dioxiranes, *etc.*[28, 33, 62, 65–77]

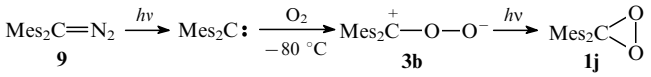


Evidence has been obtained for the formation of unsubstituted dioxirane **1e** in the oxidation of carbene **:**CH_2 in an oxygen-containing matrix.[78] Photocyclisation of propynal *O*-oxide **3a** to give propargyldioxirane **1i** has been reported.[79]



Despite the fact that photooxidation of diazo compounds made it possible to detect several dioxiranes, this method for their synthesis has not found wide application because it requires thorough control of the photolysis conditions, temperature and the solvent (in order to avoid side reactions of carbenes) and because carbene and carbonyl oxide are unstable. The lifetimes of these species have to be sufficiently long and, in addition, photodecomposition of the diazo compound and photocyclisation of carbonyl oxide have to occur at those wavelengths where the dioxirane is stable in order to avoid its rearrangement into an ester. Until recently, dioxiranes obtained in this way could be studied only at low temperatures.

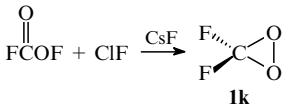
However, in 1994, Sander *et al.*[80] succeeded in preparing the relatively stable dimesityldioxirane **1j** at quite plausible temperatures (about −80 °C). This compound was synthesised from dimesityldiazomethane **9** *via* the corresponding carbonyl oxide **3b**, the lifetime of which is several orders of magnitude longer than that of diphenylcarbonyl oxide.



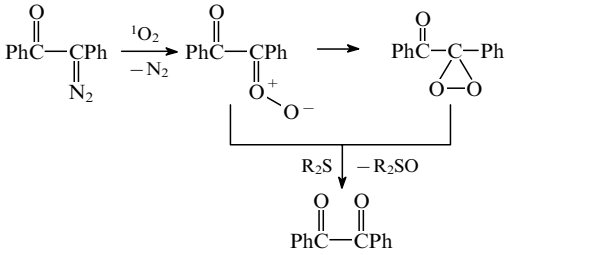
An advantage of this system is that the dioxirane **1j** does not absorb in the spectral range needed to synthesise it. Later, Sander *et al.*[81] proposed several convenient procedures for the synthesis of dimesityldioxirane **1j**, resulting in the formation of this compound both in solution and in the crystalline state (melting point 62–64 °C).

c. Formation of dioxiranes in other peroxide systems

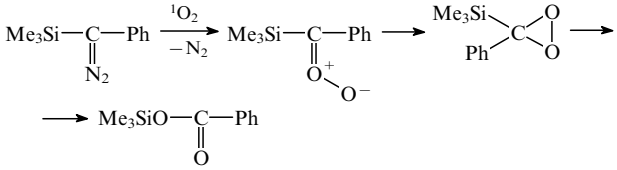
Among various non-peroxide methods for the synthesis of dioxiranes, studies by Russo and DesMarteau [82, 83] deserve attention. They prepared difluorodioxirane **1k**, which is stable in the gas phase at room temperature over a period of several days, and characterised it by IR spectroscopy (the boiling point of the dioxirane **1k** is −80 to −90 °C, and the melting point is < −160 °C).



In some studies dioxiranes are considered to be possible intermediates in various chemical reactions. Thus in a study of the oxidation of acyl-substituted diazo compounds by singlet oxygen, Ando *et al.*[84, 85] concluded that this reaction can give both carbonyl oxide and dioxirane; it is these compounds that are responsible for the oxidation of sulfides.



Apparently, the photosensitised oxidation of phenyl(tri-methylsilyl)diazomethane with singlet oxygen also occurs *via* a dioxirane.[86]



Dioxiranes have been suggested as intermediates in the decomposition of α-azo hydroperoxides by pyridine,[87–90] oxidation of some azines [91] and ylides [92, 93] by singlet oxygen, in the reaction of the $^T(F_2C{:})$ carbene with O_2 in the presence of alkenes [94] and in the decomposition of some endoperoxides.[95, 96]

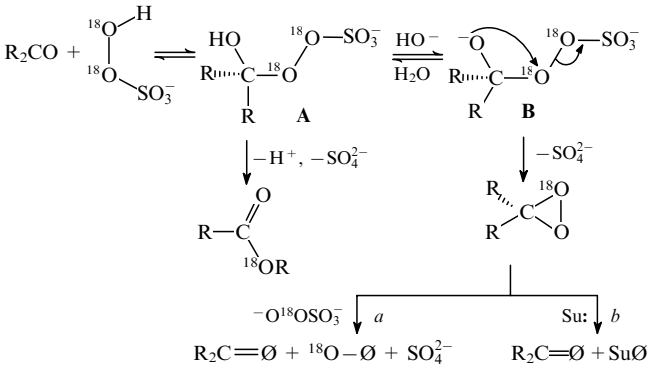
Steinfatt,[97–100] who observed chemiluminescence during the reaction of geminal dichloro-derivatives of hydrocarbons with Na_2O_2, suggested that luminescence is due to a dioxirane formed as the key intermediate in this reaction. A dioxirane intermediate has been postulated to interpret the mechanism of bioluminescence of bacteria.[101] Recently, we suggested that chemiluminescence in the Ph_2CCl_2 – NaOH – H_2O_2 system, which is similar to the Steinfatt systems, is also associated with a dioxirane [12] (studies

dealing with the chemiluminescence of dioxiranes are described in greater detail in Section V).

2. Peroxide method for the synthesis of dioxiranes

Despite the existing successful examples where dioxiranes have been synthesised using the procedures described above, the peroxide method for the synthesis of dioxiranes is still the most convenient and the most widely used in synthetic practice. The discovery of this method was preceded by the publication of Montgomery,[102] who found that some ketones catalyse decomposition of monoperoxysulfuric acid (Caro's acid) and accelerate various oxidative transformations involving this acid. Montgomery suggested that dioxirane is formed as an intermediate in the catalytic decomposition of H_2SO_5. Somewhat later,[103–108] the presence of dioxirane in the H_2SO_5–R_2CO system has been proved by the isotopic dilution method using the ^{18}O isotope (Scheme 2).

Scheme 2



Su: is substrate, Ø is 50%^{16}O and 50%^{18}O.

It was in the above series of studies [103–107] that the researchers showed for the first time that dioxirane itself is also a strong oxidant, which is able, for example, to accomplish highly efficient epoxidation of alkenes (Scheme 2, pathway *b*). The reactions were carried out *in situ* in the system 'KHSO$_5$ [or $K_2SO_4 \cdot KHSO_4 \cdot 2KHSO_5$ (oxone)]–ketone–substrate (Su:)' at pH ≈ 7.5. The necessity of maintaining a constant pH value is due to the fact that pH > 7.5 leads to an increase in the concentration of the $^-O-OSO_3^-$ dianion, which reacts with dioxirane (Scheme 2, pathway *a*) to destroy the latter, whereas at pH < 7.5, deprotonation of intermediate **A** is virtually terminated and the formation of intermediate **B** and then of dioxirane becomes unlikely.

However, the main difficulty lay in the fact that dioxirane itself could exist *in situ* only together with the corresponding ketone, oxone, H_2O and other reagents needed to maintain pH; of course, this created certain problems hampering the use and investigation of dioxirane. Therefore, the main challenge was to isolate dioxirane from the reaction mixture. This was attained in 1985 by Murray and Jeyaraman,[1] who developed a procedure for the preparation of the individual dioxirane **1a** and some other alkyldioxiranes (ethylmethyldioxirane, diethyldioxirane, methyl-n-propyldioxirane, n-butylmethyldioxirane, *etc*.). This study was the first to make dioxiranes accessible for investigations and to open up the way for their extensive use.

A key point in the Murray method [1] was the fact that the reaction of oxone with the initial ketone was carried out in a stream of an inert gas and under a slightly reduced pressure; this made it possible to separate dioxirane as a vapour, which was then collected in cooled traps. Later, this procedure was somewhat modified;[109–111] however, the basic principle remained the same. This method was also used to prepare the dioxirane **1b**,[111] which proved even more reactive than **1a**.

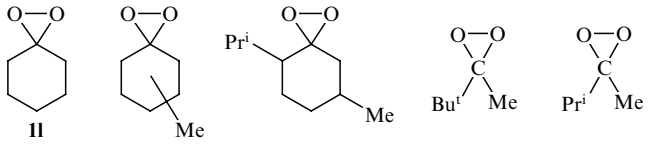
It is noteworthy that the Murray procedure for the preparation of dioxiranes is fairly simple and can be performed almost in any laboratory (see, for example, Ref. 110). It should only be borne in mind that the reactants need to be thoroughly purified from possible impurities in order to avoid decomposition of dioxirane (see Section III) and that drying agents, if required, should be chosen with caution because it has been noted (see, for example, Refs 2, 112 and 113) that some drying agents affect the stability of the dioxirane **1a** and shorten its lifetime. Therefore, when the purpose of the study does not imply thorough drying, it is better to avoid this procedure and to remove water by decanting the solution from H_2O crystals at a low temperature (−75 °C).

The drawbacks of the peroxide Murray method are that it yields dioxiranes only in small amounts and that the initial ketone is distilled from the reaction mixture together with the dioxirane. Thus the concentrations of the dioxiranes **1a** and **1b** in the initial ketone are only 0.06–0.12 and 0.65–0.82 mol litre^{-1}, respectively. The concentrations of other alkyldioxiranes prepared by this procedure are even lower.[1] The attempts to increase the concentration of the dioxirane **1a** by varying the synthesis conditions and the experiments on its distillation failed.[3] Thus, acetone is an immutable 'companion' of the dioxirane **1a** in all its chemical transformations.

However, in the case of the dioxirane **1b**, the initial ketone, 1,1,1-trifluoropropanone (TFP), has been completely separated. For this purpose, the dioxirane obtained was dissolved in the corresponding solvent (CCl_2FCClF_2, CCl_4, CH_2Cl_2, *etc*.) and the solution was washed with doubly distilled water. The initial ketone, which reacts with water forming a hydrate, is extracted into the aqueous phase, whereas the dioxirane **1b** remains in the organic phase.[114] To obtain more concentrated solutions, frozen solutions of the dioxirane **1b** (77 K) were slowly evaporated (< 10^{-2} Torr) and then recovered in cooled traps.[114]

A similar concentration procedure has been developed by Messeguer *et al*.[115,116] for the dioxirane **1a**. The method is based on the fact that **1a** is more lipophilic than acetone. Although complete removal of acetone was not attained in this case, extraction of an acetone solution of the compound **1a** with an organic solvent (CCl_4, CH_2Cl_2, $CHCl_3$) followed by washing of the organic extract with a phosphate buffer (pH 7) made it possible to obtain more concentrated solutions of the dioxirane **1a** (0.23–0.35 mol litre^{-1}).

In conclusion, another study by Murray *et al*.[117] should be mentioned; the researchers reported a procedure for preparation of a number of dioxiranes (0.2–0.8 mol litre^{-1}) from ketones poorly soluble in water.



1l

Unfortunately, the peroxide method described above cannot be used for the synthesis of 'heavier' dioxiranes with bulky substituents, in particular, phenyl-substituted dioxiranes.

3. Identification and analysis of dioxiranes

NMR, UV and IR spectroscopy are the most informative methods, used most often to identify dioxiranes. As can be seen from Table 1, common features of dioxiranes include a characteristic signal (δ 100 ppm) for the carbon atom bound to the peroxide group in the ^{13}C NMR spectrum and a relatively weak absorption band in the near UV region (λ = 300–380 nm), ending in the visible region, which is due to the 'forbidden' n–π^* transition and is responsible for the pale yellow colour of dioxirane solutions (Fig. 1).

Configurations of dioxiranes are determined using their reactions with methyl phenyl sulfide and triphenylphosphine, iodometric titration and spectrophotometry (the latter method is applicable provided that the extinction coefficient of dioxirane is known).

Table 1. Main spectroscopic characteristics of some dioxiranes (the data were taken from Refs 1, 3, 81, 109, 111 and 117).

Dioxirane	T/ °C	δ /ppm				λ_{max} /nm	ε /litre mol^{-1} s^{-1}
		^{1}H	^{13}C	^{17}O	^{19}F		
Me_2C(O)(O) **1a**	0	1.65	102.3 (COO); 22.69 [a] (Me)	302 [b]		335	10
Me, F_3C, C(O)(O) **1b**	−20	1.97 [c]	97.32 (COO); 14.51 [c] (Me); 122.2 (CF_3)	297 [c]	−81.5 [d]	347	9 [c]
Mes_2C(O)(O) **1j**	−40	2.19 (12H, *o*-Me) 2.24 (6H, *p*-Me) 8.82 (4H, aryl)	103.0 (COO); 20.9 (*p*-Me); 21.6 (*o*-Me); 130.6 (*m*-C)			206, 274	$10^{4.6}$, $10^{3.2}$
Me, Et, C(O)(O) **1m**	–		103.9 [e] (COO)			333	126[e]
O, O **1l**	−17		104.51 (COO) 33.36, 24.68 (signals of the other carbon atoms)			345	

[a] ^{13}C NMR spectra were recorded relative to Me_4Si. [b] Acetone labelled by the ^{17}O-isotope was used as the initial ketone. [c] The measurements were performed in 1,1,1-trifluoropropanone. [d] ^{19}F NMR spectra were recorded relative to $CFCl_3$. [e] The measurements were performed in methyl ethyl ketone.

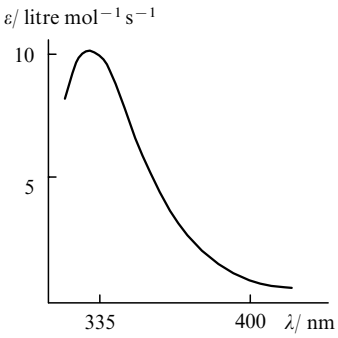
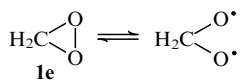


Figure 1. Absorption spectrum of the dioxirane **1a**.

4. Thermochemistry of dioxiranes

The data obtained by microwave spectroscopy [41–44] for unsubstituted dioxirane **1e** indicate that this compound contains the longest peroxide bond (1.52 Å) among such bonds known so far. This strained character of the peroxide ring should favour the homolytic cleavage of the O–O bond to give the biradical intermediate



(3)

According to theoretical calculations, the activation energy of this process is ~15 kcal mol^{-1}, whereas the activation barrier to the back reaction (cyclisation) is negligibly small,[4] < 1 kcal mol^{-1} (note that in a study [118] which is considered in more detail below, the activation energy of cyclisation of the biradical has been suggested to be ~10 kcal mol^{-1}). The results of studies of various energy states of dioxirane **1e**, the corresponding biradical and the carbonyl oxide indicate that dioxirane **1e** cannot pass into carbonyl oxide without substantial energy expenditure, because the energy of the carbonyl oxide is much higher.[4] Indeed, no examples of this transformation are known. The back reaction, which also requires additional activation energy, equal to ~22 kcal mol^{-1}, occurs on irradiation of dioxiranes.[28, 29, 33, 62, 65–77, 80, 81]

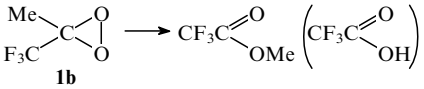
III. Thermal decomposition of dioxiranes

Despite the substantial progress attained in the studies of oxidative processes of dimethyl- (**1a**) and methyl(trifluoro-methyl)dioxiranes **1b**, the behaviour of these compounds in solutions in the absence of easily oxidisable substrates is still enigmatic and contradictory and remains the least studied aspect in the chemistry of dioxiranes. At present, facts are being accumulated along this line; however, they are often fairly contradictory. In fact, there is still no general agreement concerning either the products of decomposition of the dioxirane **1a** or its stability (the values for the time needed for decomposition of the dioxirane **1a** at room temperature reported in the literature [109, 112, 119] range from 7 h [109] to 26 days [112]).

This situation is due to the properties of dioxiranes; apparently, their decomposition is a complex process depending on numerous factors and conditions.

1. The products and mechanism of decomposition of methyl(trifluoromethyl)dioxirane

Decomposition of methyl(trifluoromethyl)dioxirane **1b** in the initial ketone gives methyl trifluoroacetate (MTFA) and trifluoroacetic acid, formed upon its hydrolysis, as the major products.[111]



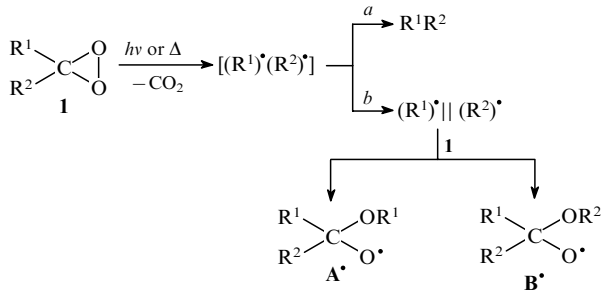
(4)

The half-life of the dioxirane **1b** in the initial ketone is ~20 h at 15 °C (at −20 °C, the decrease in the concentration is ~6% over a period of 48 h).[111] In addition, it was noted [111] that decomposition of the dioxirane **1b** at 0 °C follows complex kinetics corresponding to a mixed first and second order.

Later, when solutions of the dioxirane **1b** in inert solvents were obtained, the full picture of its decomposition occurring at elevated temperatures or on exposure to UV radiation was identified.[114] Whereas at low temperatures the dioxirane **1b** is

rather stable in inert solvents (at −20 °C, the decrease in its concentration in CCl_4 or CH_2Cl_2 is 5%–6% over a period of 168 h), at elevated temperatures (60 °C, CCl_4), it decomposes by almost 50% within 30 min.[114] Thorough investigation of the products of thermolysis (60 °C) and photolysis of solutions of the dioxirane **1b** free from the corresponding ketone showed that under these conditions, decomposition occurs by a radical chain mechanism[114] and affords MTFA, trifluoromethyl acetate (TFMA) and methyl acetate (MA). Apart from the esters listed above, the reaction mixture contains acetic and trifluoroacetic acids, which, in the opinion of the authors cited,[114] have resulted from hydrolysis of TFMA and trifluoromethyl trifluoroacetate (TFMTFA), respectively. In addition, evolution of CO_2 was noted in all cases. These facts and the fact that in the presence of O_2, the photolytic process is substantially retarded and the formation of esters is markedly depressed provide strong evidence for the chain radical mechanism of decomposition of the dioxirane **1b** (Scheme 3).

Scheme 3

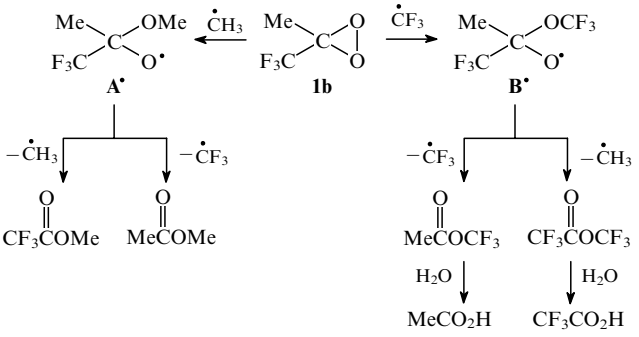


R^1 = Me, R^2 = CF_3.

In conformity with the Scheme 3, decomposition of methyl(trifluoromethyl)dioxirane gives rise to the radical pair [$\dot{C}H_3$ $\dot{C}F_3$], which then either recombines according to pathway *a* or generates free radicals $\dot{C}H_3$ and $\dot{C}F_3$ (pathway *b*); these radicals, in turn, attack dioxirane yielding alkoxyl radicals **A**$^{\bullet}$ and **B**$^{\bullet}$. Pathway *a* is realised when methyl(trifluoro-methyl)dioxirane is photolysed in a matrix. In this case (unlike experiments in solution), 1,1,1-trifluoroethane is a major product of decomposition of dioxirane.

Radicals **A**$^{\bullet}$ and **B**$^{\bullet}$ undergo β-cleavage to give esters with the regeneration of alkyl radicals, which carry the chain (Scheme 4).[114]

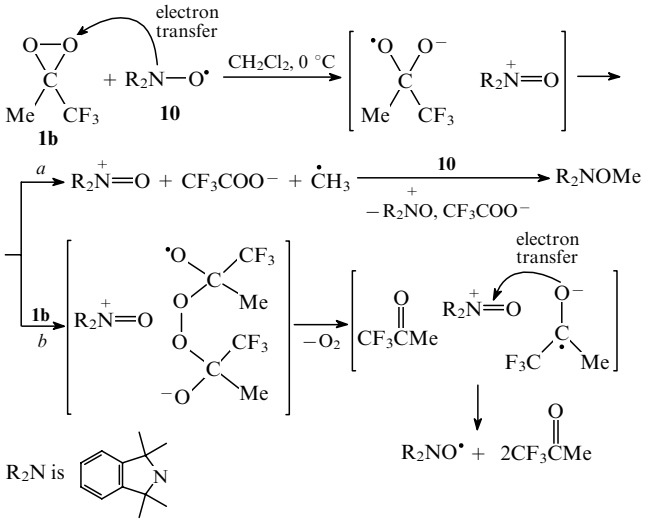
Scheme 4



It is of interest that no radical chain processes are involved in the vacuum flash pyrolysis (500 °C) of the dioxirane **1b**,[114] which gives only MTFA. Apparently, in this case, dioxirane simply isomerises to ester according to reaction (4).

The radicals formed upon decomposition of the dioxirane **1b** were detected at low temperatures using 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl **10** as a spin trap.[120] However, the adduct of the nitroxide **10** and the $\dot{C}H_3$ radical is formed apparently *via* the dioxirane radical anion, resulting from the transfer of an electron from the nitroxide **10** to the dioxirane **1b** (Scheme 5, pathway *a*).[120] Yet another channel of consumption of the radical anion is pathway *b*.

Scheme 5

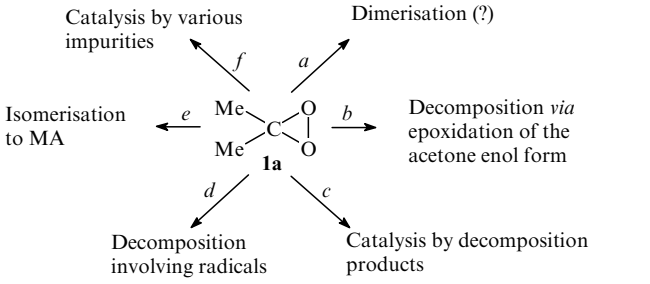


The decomposition of the dioxirane **1b** can also be induced by various impurities. Thus it has been noted[121] that the presence of even traces of metals can cause rapid decomposition of dioxiranes. Messeguer *et al.*[122] have found that catalytic amounts of dialkyl ethers (*e.g.*, diethyl or dihexyl ether) induce rapid decomposition of the dioxirane **1b** in a radical chain process. This finding appears very important because the same researchers reported[122] that these ethers are contained in the initial TFP even after distillation. However, they can be removed. Thus when TFP is washed with water and an inert solvent, the ethers are accumulated in the organic phase, whereas TFP passes into the aqueous phase as hydrate.

2. The products, kinetics and mechanism of decomposition of dimethyldioxirane

Several routes for decomposition of dioxiranes **1a** can be found in the literature (Scheme 6).

Scheme 6



Evidently, the realisation of one or another channel of transformation of the dioxirane **1a** depends on a whole series of conditions such as temperature, the content of O_2, the presence of impurities, *etc*. Some of these factors can be controlled; the influence of some other factors can be reduced (for example, by thorough purification of the initial compounds). Table 2 contains data on the products of decomposition of the dioxirane **1a** and on the reaction mechanisms that have been invoked by the researchers in order to interpret the results obtained and that are considered in detail below.

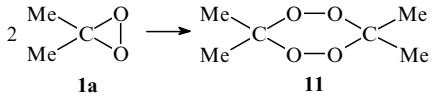
Table 2. Products of decomposition of dimethyldioxirane (**1a**) under various conditions.

Reaction conditions	Proposed mechanism (Scheme 6)	Decomposition products	Ref.
Room temperature, no special purging with oxygen or an inert gas	*a*	diperoxide **11**	1
	b	hydroxyacetone (**12**) + MA [a]	119
	the mechanism is not discussed	MA [a]	112
Vacuum flash pyrolysis, 150–180 °C	*e*	MA	112
In boiling acetone	*d*	MA + 1-(acetyloxy)propan-2-one	112
Decomposition in the presence of BF_3	pathways *b* and *e* occur in parallel	MA + **12**	112
Room temperature	*e*	MA	15
Decomposition in the presence of CCl_3Br, 20 °C	*d*, *e* and *f*	MA [b], 1-(acetyloxy)propan-2-one, CH_3CO_2H, CH_3Br, $CHCl_3$, CH_3OH, $ClCH_2C(O)CH_3$	37
Decomposition in the presence of the Ru(II) tris(bipyridine) complex, 40 °C	*e* (see [c])	MA	15

[a] Some quantity of MA was already present in the initial solutions of **1a**. [b] Methyl acetate was the major product. [c] In this case, we are dealing with catalysed isomerisation of dioxirane to MA according to the electron transfer mechanism (see Section V).

a. Dimerisation of dimethyldioxirane

The first data on the products of decomposition of dimethyldioxirane **1a** were published in 1985. Murray *et al.*[1] reported on the conversion of the dioxirane **1a** into cyclic diperoxide **11**:

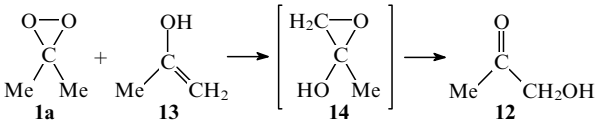


1a **11**

Later, however, they were unable to reproduce their own results [112] and suggested that compound **11**, which they had observed previously, must have been formed as a side product during the synthesis of dioxirane.

b. Decomposition with participation of the enol form of acetone

Decomposition of the dimethyldioxirane **1a** at room temperature has been reported [119] to give hydroxyacetone **12** together with a minor amount of methyl acetate. It was noted [119] that solutions of dioxirane always contain some MA, which appears apparently during the synthesis of dimethyldioxirane. Based on this finding, a decomposition mechanism has been proposed, the key stage of which includes the reaction of the dioxirane **1a** with the enol form of acetone **13** followed by rearrangement of the resulting epoxide intermediate to hydroxyacetone **12**.



1a **13** **14** **12** (5)

However, the possible formation of the hydroxy ketone **12** upon direct insertion of an oxygen atom into the C–H bond of acetone or in a free-radical process also cannot be ruled out.[119]

The contribution of reaction (5) to decomposition of the dioxirane **1a** increases in the presence of BF_3. In the opinion of Murray and Singh,[112] boron trifluoride exerts a dual effect: on the one hand, it increases the rate of conversion of **1a** into MA and, on the other hand, it favours an increase in the concentration of the enol **13**, which then reacts with **1a** [reaction (5)] to give hydroxyacetone (see Table 2).

It was also found that solutions of the dioxirane **1a** are sensitive to the presence of bases; the addition of KOH to a solution of dioxirane results in its rapid decomposition, which follows first-order kinetics.[119] A similar situation has been observed in the case of a solution of deuterated dioxirane **1a**, which proved to be more stable than the non-deuterated compound ($k_H/k_D \sim 4$).[119]

c. Catalysis by decomposition products

Many researchers (see, for example, Refs 109, 112, 118, 119, 123) have noted that at high concentrations ($\geqslant 0.06$ mol litre^{-1}), decomposition of the dimethyldioxirane **1a** does not follow first-order kinetics; instead, it has a fairly long induction period, which is followed by rapid decomposition (Fig. 2). It was found that the higher the temperature and the dioxirane concentration, the shorter the induction period.[118, 123] It was suggested that reaction products have a catalytic effect on the decomposition of the dioxirane **1a**. Indeed, comparison of curves *2* and *3* in Fig. 2 shows that **1a** decomposes much faster in the presence of decomposition products. Unfortunately, the products of decomposition of **1a** were not specified in the study cited.[118]

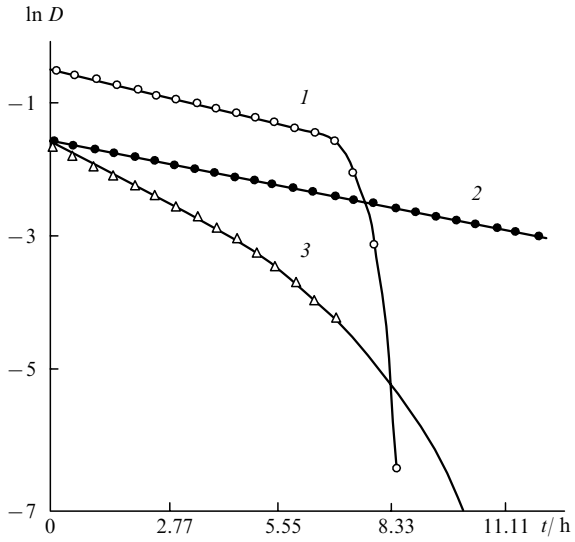


Figure 2. Kinetic curves for the consumption of dimethyldioxirane **1a** in acetone at 50 °C (solutions of **1a** in acetone were used without preliminary dehydration).[118]
The initial concentration of the dioxirane **1a** (mol litre^{-1}): (*1*) 0.12, (*2*) 0.02, (*3*) 0.02 (in the presence of the products formed upon decomposition of 0.12 mol litre^{-1} of a solution of the dioxirane **1a**).

When the concentration of the dioxirane **1a** is low (0.02 mol litre^{-1}), its decomposition follows first-order kinetics (Fig. 2, curve *2*).[112, 118, 123] This fact was used [118] to determine the activation parameters of the decomposition of **1a** in the temperature range 25–75 °C: $\log k = 12.4 - 24.9/(2.3RT)$. Thus, at 25 °C, $k = 1.53 \times 10^{-6}$ s^{-1}, and the activation energy of decomposition of the dioxirane **1a** is about 9–10 kcal mol^{-1} higher than the value calculated theoretically ($\sim$15 kcal mol^{-1}) for unsubstituted dioxirane **1e**.[4] The latter result was interpreted [118] as being due to

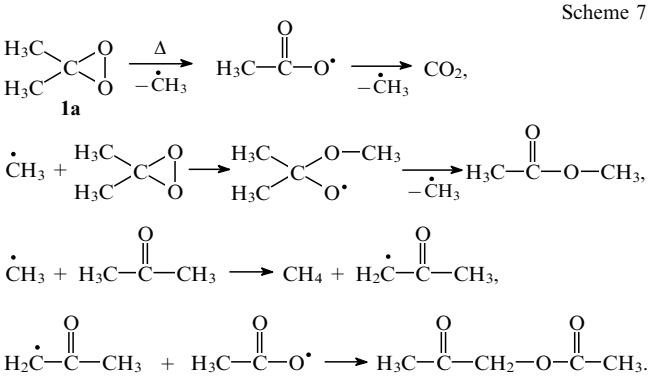
the possible underestimation of the activation energy for the back cyclisation of the dioxirane biradical [see reaction (3)]; the researchers cited estimated [118] this value to be actually ~10 kcal · mol^{-1}.

According to our data,[123] a major product of decomposition of the dioxirane **1a** (see Table 2), namely, methyl acetate (1×10^{-2} mol litre^{-1}) actually accelerates the reaction; however, this effect is insignificant: the ratio of the effective rate constants for decomposition of **1a** in the presence and in the absence of MA is ~1.4. Autocatalytic decomposition might account for one channel of consumption of the dioxirane **1a**, occurring in parallel with other channels such as radical chain decay and isomerisation to give MA.

d. Radical chain decay

Singh and Murray [112] showed that radical chain processes play an important role in the decomposition of the dimethyldioxirane **1a**. Analysis of the products resulting from refluxing **1a** in acetone and in a mixture of acetone with other ketones (butan-2-one, pentan-2-one, *etc.*) demonstrated the presence of various esters, apart from MA, the formation of which could be explained only in terms of a radical chain mechanism. It was also found that when the compound **1a** is refluxed in an acetone solution, the rate of the process, the products formed and the product ratio depend substantially on whether or not O_2 is present in the system; in fact, under an atmosphere of O_2, **1a** decomposed only by 27% over a period of 2 h, whereas under argon the dioxirane completely decomposed over a period of 10–15 min under similar conditions.[112] Based on their own results and on the data on decomposition of the dioxirane **1b** obtained by Adam, Curci, *et al.*,[114] Singh and Murray [112] proposed a scheme for radical chain decay of dimethyldioxirane **1a** in acetone (Scheme 7).

Scheme 7



Scheme 7 well accounts for the inhibitory effect of O_2 on the rate of decomposition of **1a**; an oxygen molecule reacts with reactive alkyl radicals, for example $\dot{C}H_3$, to convert them into stable peroxyl radicals and thus inhibits the chain process. Our experimental data [13] are also in good agreement with the results obtained by the researchers cited above:[112] complete decomposition of dimethyldioxirane **1a** in solvents freed from oxygen (46 °C) occurs 4 times faster than under ordinary conditions (the kinetic isotope effect $k_H^{eff}/k_D^{eff} \approx 3.12$).

As in the case of the dioxirane **1b**, the reaction of **1a** with nitroxide trap **10** affords the adduct R_2NOCH_3.[120]

Generally speaking, nitroxides [*e.g.*, tetramethylpiperidyloxyl (TEMPO)] are not convenient traps for the radical intermediates formed during dioxirane decomposition, because they are able to react directly with **1a** and **1b** thus inducing their consumption in a radical chain process; for TEMPO, this is illustrated in Scheme 8.[124]

When the dioxirane **1a** was made to react (0–56 °C) with a spin trap, *N*-*tert*-butyl-*C*-phenylnitrone **15**, the formation of the nitroxide **16** was detected based on the EPR signal (a triplet of doublets with splitting constants at the N and H atoms equal to 13.5 and 2 Œ, respectively) [125] (Fig. 3). This signal was

Scheme 8

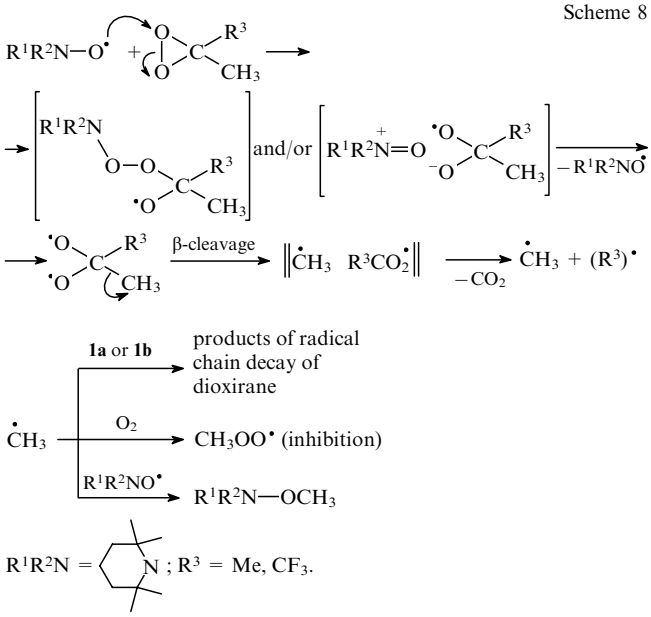
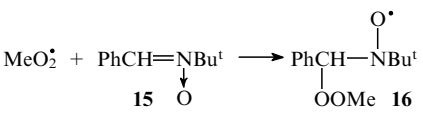




Figure 3. EPR spectra recorded in the dioxirane **1a** – nitrone **15** system at 40 °C within 5 (*a*) and 15 min (*b*) after the sample has been placed in the spectrometer resonator. The initial concentrations of the dioxirane **1a** and the nitrone **15** are 0.03 and 0.045 mol litre^{-1}, respectively.

assigned [126, 127] to an adduct of the nitrone **15** with the peroxyl radical $MeO_2^{\bullet}$, *i.e.* to the compound **16**.



The formation of $MeO_2^{\bullet}$ was explained by assuming that the methyl radicals $^{\bullet}CH_3$, generated upon decomposition of **1a**, react with O_2 molecules (the rate constant for the reaction of the $^{\bullet}CH_3$ radicals with O_2 is $\sim 5 \times 10^9$ litre mol^{-1} s^{-1}).[128] However, the formation of these radicals upon direct interaction of the dioxirane **1a** with the nitrone **15** also seems quite likely.

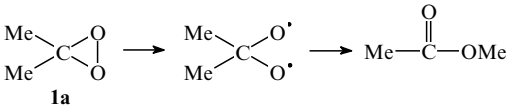
It is of interest that ~10 min after the EPR signal due to the adduct **16** has arisen, one more triplet with the splitting a_N = 8.1 Œ appears in the EPR spectrum (Fig. 3); this signal has been attributed [125] to benzoyl *tert*-butyl nitroxide, the formation of which was explained by rearrangement of the adduct **16**.[126, 127, 129, 130]

The unusual shapes of the kinetic curves for the decay of dioxirane **1a** (see Fig. 2) can also be interpreted in terms of a radical chain mechanism. Indeed, the presence of an induction period under ordinary conditions, *i.e.* without additional purging of the system by an inert gas or O_2, may be associated with the inhibitory effect of oxygen, which is always originally present in a solution (thus the concentration of O_2 in acetone is 6.8×10^{-3} mol litre^{-1}).[131] The reaction of the reactive alkyl radicals, generated upon decomposition of dioxirane, with O_2 molecules decreases the oxygen concentration in the system and results in

the consumption of **1a** in a radical chain process, which is manifested as a sharp acceleration of the reaction. This is quite consistent with the decrease in the induction period following an increase in the temperature [118] and also with the substantial effect of argon. Even when the concentration of the dioxirane **1a** is relatively low (0.03 mol litre^{-1}) and the temperature is moderate (20 °C), the induction period in the reaction performed under argon decreases to ~150 min.[124] It comes as no surprise that the dioxirane decomposition under an atmosphere of O_2, which inhibits the radical chain process, strictly follows first-order kinetics irrespective of the initial dioxirane concentration or temperature (30–49.5 °C).[132]

e. Isomerisation of dimethyldioxirane to methyl acetate

Although arguments in favour of the radical mechanism of decomposition of the dioxirane **1a** are quite forcible, the existence of a parallel channel of the decomposition of **1a**, namely, its isomerisation to MA *via* a biradical intermediate, can also be considered to be proven.



(6)

It was found [14] that reaction (6) occurs under conditions of photolysis of the dioxirane **1a** in a matrix (77 K) (isomerisation is also a major pathway of the low-temperature phototransformation of some other dioxiranes [33]). In addition, at higher temperatures, (T = 150–180 °C, vacuum flash pyrolysis), reaction (6) is regarded as the major pathway for decomposition of dimethyldioxirane (remarkably, under these conditions some **1a** remains intact!).[112] Apparently, rearrangement to give MA is the main route of decomposition of the dioxirane adsorbed on the Silipor surface from the gas phase.[11, 16]

However, it is reasonable to suggest that decomposition of the dimethyldioxirane **1a** in solution also involves reaction (6). Its contribution depends most likely on the temperature and other experimental conditions. Due to the influence of impurities and at elevated temperatures, which promote the occurrence of parallel routes of the radical chain decay of the dioxirane **1a**, the fraction of isomerisation should decrease. However, it has been shown experimentally that even under conditions most favourable for a radical chain process (46 °C, absence of O_2), reaction (6) still does occur, because it is this reaction that is responsible for the chemiluminescence observed under these conditions [13] (this aspect is considered in greater detail in Section V). In our opinion, the contribution of reaction (6) markedly increases at lower temperatures; apparently, at room temperature and below room temperature, it becomes the major route for the dioxirane consumption.

Note that reaction (6) can also be induced by a catalytic influence of various compounds. Thus ruthenium tris(bipyridine) complex $Ru(bipy)_3^{2+}$ and some polyaromatic hydrocarbons, which act as activators of the CL arising by the chemically initiated electron-exchange luminescence (CIEEL) mechanism, catalyse isomerisation of dioxirane.[6, 10, 12, 15, 16, 123] Apparently, the Silipor surface also functions as a catalyst.[11, 16]

e. Catalysed (induced) decomposition of dimethyldioxirane by impurities

Some impurities have an exceptionally significant influence on the stability and the decomposition mechanism of the dioxirane **1a**. These impurities include some metals, traces of dehydrating agents (*e.g.*, molecular sieves,[112] $MgSO_4$, *etc.*) and reactive compounds present in the initial acetone or introduced into a solution of the dioxirane **1a** from the reaction vessel at the stage of its synthesis. Murray [2] noted that the lifetime of dioxirane depends on the pre-history of the sample and can be sensitive to admixtures of the dehydrating agent used (*e.g.*, Na_2SO_4).

An example of dioxirane decomposition induced by impurities has been reported.[37] It was shown that the stability of dimethyldioxirane **1a** is substantially affected by the addition of CCl_3Br. Whereas decomposition of the dioxirane **1a** under ordinary conditions follows first-order kinetics ($k = 6.2 \times 10^{-6}$ s^{-1}), the addition of CCl_3Br, especially with simultaneous removal of O_2 from the system, sharply accelerates the process (Fig. 4), the product composition leaving no doubt as to the participation of free radicals in the dioxirane decomposition in the presence of CCl_3Br[37] (Scheme 9).

Presumably,[37] CCl_3Br can also participate in the formation of a biradical-ion pair with the dioxirane, resulting from transfer of an electron from the bromide to **1a**. The subsequent reverse electron transfer from the radical anion to the radical cation increases the concentration of biradical **A** and, hence, the probability of formation of the $\dot{C}H_3$ radical from it.

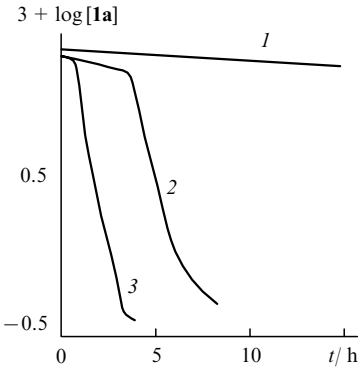
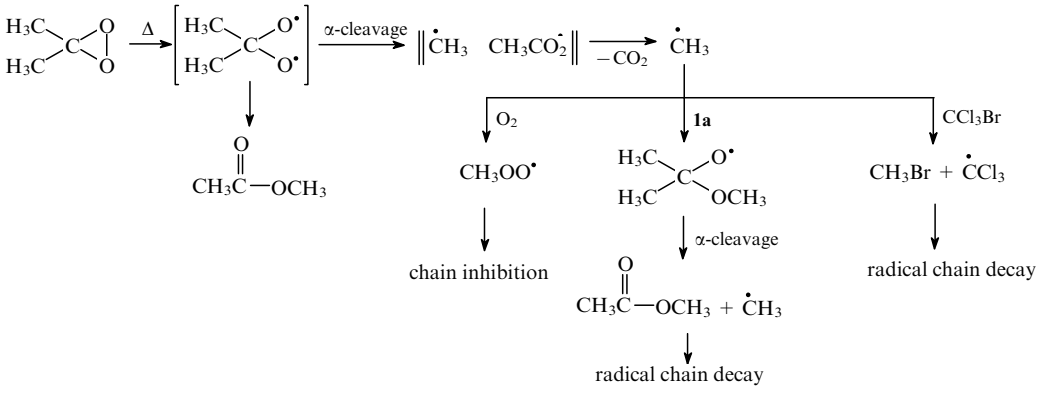
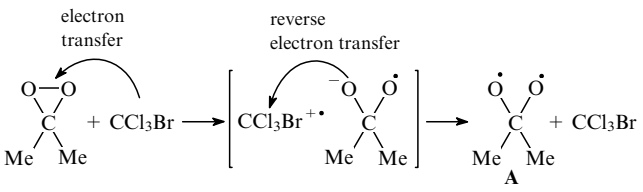


Figure 4. Kinetics of decomposition of dimethyldioxirane (**1a**) in the absence (*1*) and in the presence (*2*, *3*) of an equimolar amount of CCl_3Br; (*2*) under atmospheric conditions, (*3*) under inert atmosphere (N_2).

Scheme 9





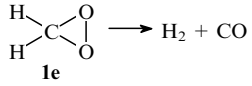
The occurrence of another parallel channel for the transformation of the biradical-ion pair, resulting in the formation of $\dot{C}Cl_3$ and $BrO^{\bullet}$ radicals, capable of participating in the radical chain decay of dioxirane, also cannot be ruled out.[37] It was noted [37, 121] that traces of metals can cause rapid decomposition of the dioxirane **1b**. Recently we have confirmed experimentally that this warning is also true for the dioxirane **1a**. It was found [15] that even catalytic amounts of ruthenium(II) $[(4-24)\times10^{-5}$ mol litre^{-1}] induce rapid decomposition of the dioxirane **1a**. It can be anticipated that other metals would also influence the stability of dioxiranes.

The stability of dioxiranes can be affected not only by traces of metals and dehydrating agents but also by organic impurities. The radical chain decay of methyl(trifluoromethyl)dioxirane **1b** in the presence of dialkyl ethers (for example, diethyl and dihexyl ethers) [122] has been already mentioned. The addition of ethers to dimethyldioxirane **1a** has a similar influence, although it is less pronounced.[122] Unfortunately, since the boiling points of dialkyl ethers and acetone are close, purification of acetone by distillation does not always lead to the desired result. The situation is aggravated by the fact that some impurities can form directly in the reaction vessel and, therefore, they can appear in a solution of dioxirane at the stage of its synthesis. For example, this concerns MA, small amounts of which get into solutions of **1a** in exactly this way.[112, 119] Impurities that have got into a dioxirane solution *via* this route can be involved in the radical decomposition of dioxirane; hence, the different lifetimes of the dioxirane **1a** synthesised by various researchers and the non-reproducibility of the kinetic data[15, 109, 112, 118, 119, 123, 132] can be due to different natures and amounts of non-controllable impurities able to accelerate decomposition of the dioxirane **1a** and promote the formation of different decomposition products (see Table 2). This resembles the situation observed in the study of the kinetic and activation parameters of decomposition of tetramethyldioxetane (TMD). In these studies, the so-called 'false solvent effect' had been discovered, manifested as a sharp acceleration of the reaction on passing from aprotic solvents (benzene, CCl_4) to alcohols (MeOH and EtOH) and poor reproducibility of the kinetic data in alcoholic solutions.[21, 133] The reason was that admixtures of transition metal ions were present even in distilled solvents.[21, 134, 135] Treatment of alcoholic solutions of TMD with complexonates improved the reproducibility, and the kinetic and activation parameters acquired values typical of aprotic solvents.

However, in the case of the dioxirane **1a**, the situation must be more complicated. Thermal decomposition of dimethyldioxirane **1a** is a complex process, its mechanism depending on numerous factors. To elucidate the extent of influence of each factor, further studies are needed.

3. Decomposition of other dioxiranes

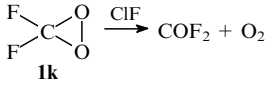
The formation of H_2 and CO is the main pathway of decomposition of gaseous unsubstituted dioxirane **1e** (-115 °C).[42, 43]



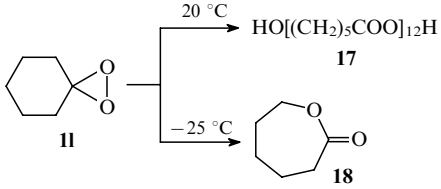
It has been noted that decomposition of dioxirane **1e** follows different channels, resulting in the formation of atomic hydrogen.[43]

Gaseous difluorodioxirane **1k** is more stable than **1e**. No decrease in its concentration has been noted over a period of 12 h at 22 °C and 15 Torr. The unusual stability of the dioxirane has become the subject of a special theoretical study.[136]

When a small amount of ClF is added to difluorodioxirane **1k**, the dioxirane is destroyed fairly rapidly to give COF_2 and O_2.[82]

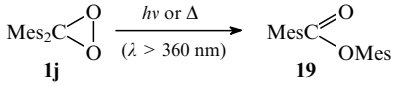


The spirocyclic dioxirane **1l** is relatively unstable:[117] at room temperature, the yellow colour, typical of dioxiranes, completely disappears in 5–10 min and the solution becomes colourless. Simultaneously, the solution substantially warms up, indicating the exothermic character of the decomposition of **1l**. Interestingly, instead of the expected lactone **18**, decomposition of the dioxirane **1l** at room temperature gives its linear oligomer **17** as the major product (90%).



However, at lower temperatures the reaction gives the lactone **18**.[117] This example clearly illustrates the statement that the reaction temperature can dictate the predominance of one or another channel of dioxirane decomposition.

Dimesityldioxirane **1j** can exist both in solution and in the crystalline state.[80, 81] In both cases, the dioxirane **1j** isomerises to the corresponding ester, mesityl mesitoate **19**:



The dioxirane **1j** is relatively stable at room temperature (its concentration decreases by 14% over two weeks) and virtually stable at -20 °C. However, on exposure to radiation, it completely isomerises into the ester **19** in several minutes.[80, 81] The stability of the dioxirane **1j** under ordinary conditions is due to the facts that its molecule is sterically hindered and the O — O bond is relatively strong and, in addition, it is the shortest (1.503 Å) among the O — O bonds in dioxiranes.[81]

IV. Dioxiranes as oxidants

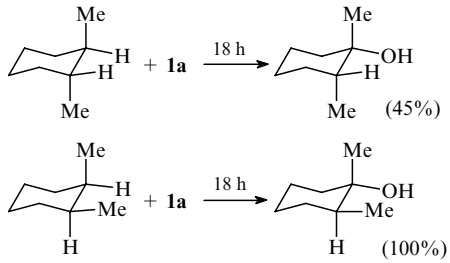
Highly selective oxidation of organic compounds of various classes is a well-studied aspect of the chemistry of dioxiranes, which is becoming more and more significant in organic synthesis. This feature, discovered even in the first studies on *in situ* generation of dioxiranes,[103–107] has fully come to light in the subsequent studies carried out using pure solutions, most often of the dioxiranes **1a** and **1b**. The main types of oxidative transformations involving **1a** and **1b** include oxidation of alkanes, alkenes, their functionally substituted derivatives containing heteroatoms (O, S, N, P), and organometallic compounds.

1. Oxidation of saturated compounds

Highly selective oxidation of saturated compounds to the corresponding hydroxy- and oxo-derivatives is one of the most important and most difficult problems in organic chemistry.[137] At present, peroxy acids, hydroperoxides, ozone, catalytic systems including transition metals and some other compounds are used most often for this purpose.[138–144] Dioxiranes, capable of oxidising selectively and under mild conditions non-activated C–H bonds in alkanes, occupy a unique place in the series of organic oxidants.

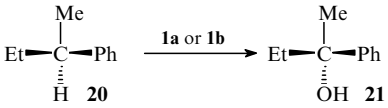
The reactions of dioxiranes with alkanes give rise to the corresponding alcohols. The oxidation of *cis*- and *trans*-1,2-

dimethylcyclohexanes by the dioxirane **1a**, reported by Murray *et al.*,[145] was among the first examples of this reaction.



A similar reaction with participation of the dioxirane **1b**, which is more reactive than **1a**, occurs much faster.[111]

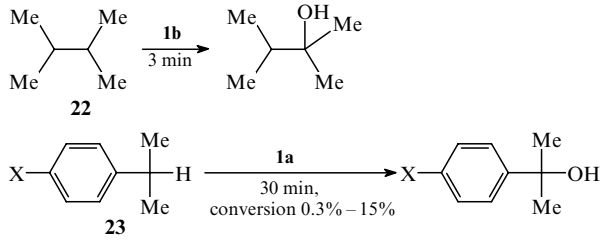
Oxidation of optically active (*R*)-(−)-2-phenylbutane **20** to (*S*)-(−)-2-phenylbutan-2-ol **21** by the dioxiranes **1a** and **1b** occurs with retention of the absolute configuration.[39,146]



(7)

In this reaction, too, methyl(trifluoromethyl)dioxirane **1b** demonstrates obvious advantages over dimethyloxirane **1a**. Thus when the dioxirane **1a** is used, a 50% degree of conversion of the alkane **20** into the alcohol **21** requires a 10-fold excess of **1a**, 2 days, and a temperature of 25 °C, whereas in the case of **1b**, 100% conversion is attained with only a 2-fold increase of the oxidant and takes 1 h at a temperature of 24 °C.

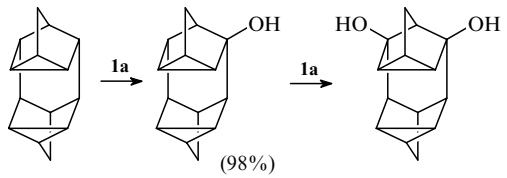
Dioxiranes have also been used successfully for the synthesis of hydroxy-derivatives of 2,3-dimethylbutane **22**, cumene **23** (X = H)[121,147,148] and its derivatives and a series of other alkanes.



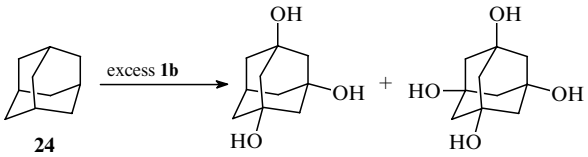
X = H, I, Me, OH, OMe, OPh, COMe.

In all cases (except for norbornane), a tertiary C–H bond in the substrate is oxidised more efficiently than secondary C–H bonds.[121] Non-activated primary and secondary C–H bonds in alkanes can also undergo selective oxidation, for example, in the presence of trifluoroacetic anhydride.[149]

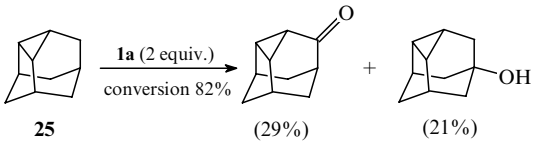
Oxidation of cage compounds yields the corresponding alcohols.[37,117,121,147,150–152] Thus oxidation of binor S by dimethyldioxirane **1a** gave rise to mono- and dihydroxy-derivatives.



Oxidation of adamantane **24** by the dioxirane **1b** gives predominantly, depending on the ratio of the reactants, either adamantan-1-ol (**1b** : **24** = 1 : 1) or adamantane-1,3-diol (**1b** : **24** = 2 : 1).[121] When **1b** was taken in a larger excess, adamantane-1,3,5-triol and adamantane-1,3,5,7-tetraol were obtained.

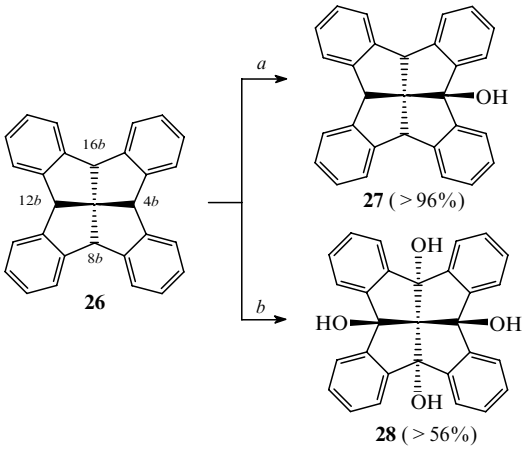


The dioxirane **1a** has also been used to oxidise adamantane[37,151] and its derivatives[147] and also 2,4-didehydroadamantane **25**[152] to the corresponding alcohols; however, it is much less reactive than **1b**.



It is of interest that the dioxirane **1l** is 4 times more reactive towards the oxidation of adamantane than **1a**.[117]

The dioxiranes **1a** and **1b** have been used to synthesise[153] hydroxy- and polyhydroxy-derivatives of several centropolyindans [triptindan, 1,1′-(*o*-phenylene)-2,2′-spirobiindan, 10-methyltribenzoquinacene, fenestrindan, *etc.*]. Thus oxidation of fenestrindan **26** by the dioxirane **1b** in the CH_2Cl_2–$CF_3C(O)Me$–Bu^tOH system affords, depending on the reaction conditions, either alcohol **27** or tetraol **28**.[153]

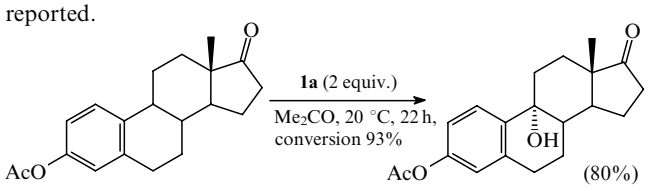


(*a*) 1.5 equiv. **1b**, CH_2Cl_2 : $CF_3C(O)Me$: Bu^tOH = 9 : 1 : 1, −10 °C, 25 min, conversion 56%;

(*b*) 10 equiv. **1b**, CH_2Cl_2 : $CF_3C(O)Me$: Bu^tOH = 5 : 4 : 1, −10°C, 25 min, conversion 97%.

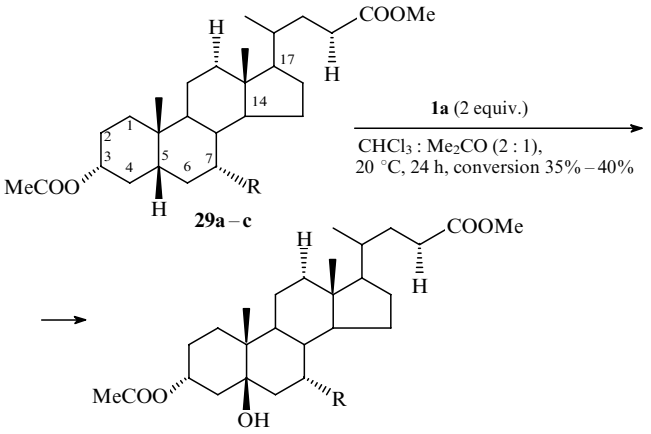
The alcohol **27** reacts with the dioxirane **1b** (1.7 equiv. of **1b**; CH_2Cl_2 : $CF_3C(O)Me$ = 9 : 1, 0 °C, 15 min, conversion 60%) to give a diol, 4*b*,8*b*-dihydroxyfenestrindan (yield > 88%).[38]

Hydroxylation of several natural products,[154–158] for example, estrone acetate,[156] by the dioxiranes **1a** and **1b** has been reported.



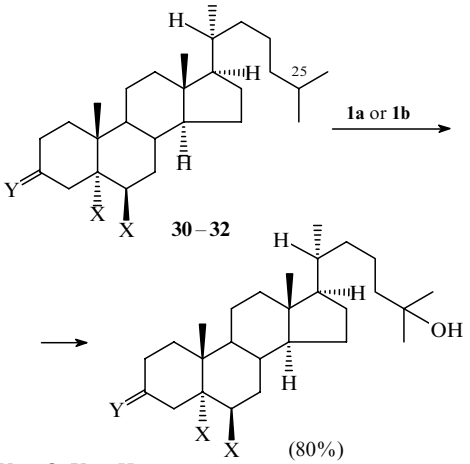
The reactions of a ~0.16 M solution of the dioxirane **1a** in a $CHCl_3$–Me_2CO mixture with a number of 5β-H-cholic acids (lithocholic **29a**, ursodeoxycholic **29b**, chenodeoxycholic acid **29c**, *etc.*) have been studied.[157] In all cases, oxidation of the C–H bond in the 5β position occurred. However, whereas lithocholic acid **29a** reacts relatively rapidly, the corresponding 5β-hydroxy-derivative being the only reaction product,[157] the acids **29b** and **29c**, containing an electron-withdrawing acetoxy group at the C(7) atom, react slowly because the 5β position is

deactivated and, apart from the 5β-hydroxy-derivative, the reaction gives the 14α- and 17α-hydroxylation products.[157]



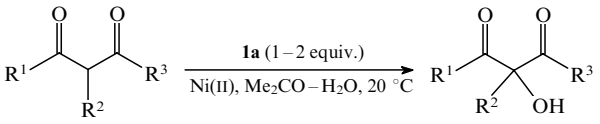
R = H (**a**), β-OCOMe (**b**), α-OCOMe (**c**).

Cholestane derivatives, for example, 5α-cholestan-3-one **30**, 3β-acetoxy-5α-cholestane **31** and 3β-acetoxy-5α,6β-cholestane **32** are also oxidised by dioxiranes at the C(25) position to give the corresponding alcohols.[158]



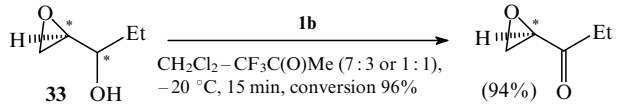
30: Y = O, X = H;
31: Y = β-OAc, H, X = H;
32: Y = β-OAc, H, X = Br.

The rate of oxidation of C–H bonds by dioxiranes can depend on 'external' factors. Whereas oxidation of 1,3-dicarbonyl compounds by even a substantial excess of the dioxirane **1a** requires about three days,[159] the same reaction carried out in the presence of Ni(II) salts as the catalyst occurs markedly faster, the reaction time being reduced to several hours.[160]

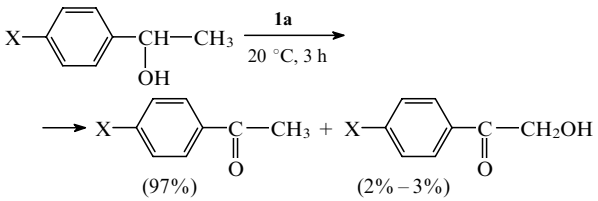


This reaction is one of the few examples of 'external' interference in the course of oxidative reactions involving isolated dioxiranes. Previously, acid catalysis has been used [161] to accomplish selective oxidation of methoxybenzenes by the dioxirane **1a** to the corresponding *p*-benzoquinones.

In some cases, the alcohols formed from alkanes are oxidised by excess dioxirane to give the corresponding ketones.[121] Several secondary alcohols have been oxidised [162] to the corresponding ketones (yields 92%–99%) by the dioxirane **1b** (oxidation of secondary alcohols proceeds more smoothly and requires less time than the oxidation of primary alcohols). A remarkable selectivity was found in the reaction of the dioxirane **1b** with 2-norborneol: the *endo*-isomer was found to be 40 times more reactive than the *exo*-isomer.[162] Oxidation of chiral α-epoxy alcohols **33** by dioxiranes does not affect the oxirane groups and occurs with retention of the configuration of the asymmetric centre adjacent to the hydroxy group.[162]

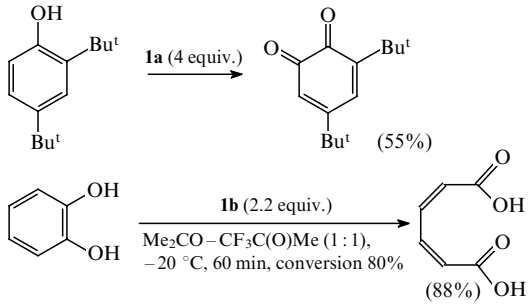


On treatment with dimethyldioxirane **1a**, several *para*-substituted α-methylbenzyl alcohols have been converted into the corresponding acetophenones in good yields.[163]

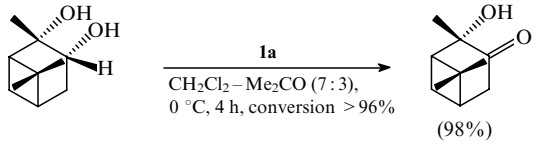


X = H, F, Cl, Br, Me, OMe, CN.

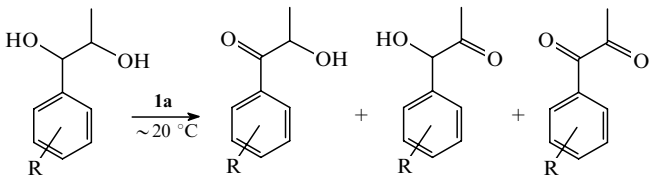
Oxidation of simple phenols by dioxiranes affords complex mixtures of products;[164] the best results were obtained in the reactions of dioxiranes with substituted phenols and catechol.[164, 165]



Aliphatic diols (including optically active ones) react with the dioxiranes **1a** and **1b** to give α-hydroxy ketones.[166, 167] It is noteworthy that oxidation of (+)-pinane-2,3-diol to (−)-2-hydroxypinan-3-one occurs with virtually complete retention of the configuration (the optical yield of the ketone is >97%).[166]

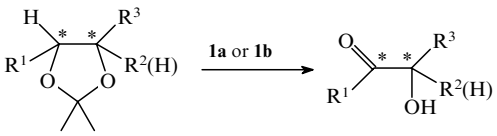


Oxidation of non-symmetrical 1,2-diols results in their complete conversion to the corresponding mono- and dioxo derivatives (regioselectivity of the process depends considerably on the nature of the substituents).[168]

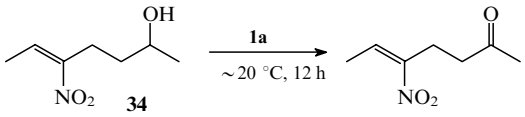


R = H, *p*-OMe, *o*-OH, *o*-NO_2, *p*-NO_2.

Optically active *O*-isopropylidene derivatives of 1,2-diols are converted into 2-hydroxy ketones, formed in high optical yields and with retention of the optical purity.[169]



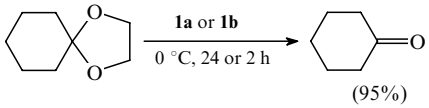
Depending on the reaction conditions and the nature of the substrate, oxidation of allylic alcohols by dioxirane **1a** occurs as either epoxidation of the double bond [106, 107] or competing oxidation of the hydroxy group to an oxo group.[170] In the oxidation of unsaturated nitro alcohols **34**, the double bond remains intact because it is deactivated by the NO_2 group.[171]



The deactivation effect is also manifested in the oxidation of nitro diols: the hydroxy group remote from NO_2 is oxidised, whereas the OH group occurring in the α- or β-position to the NO_2 group remains intact.[171]

When dioxiranes are made to react with allyl hydroperoxides, the corresponding epoxy hydroperoxides are formed.[172]

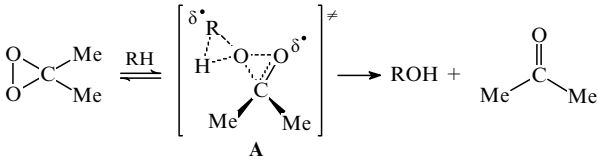
Oxidation of aliphatic esters with the dioxirane **1b** affords oxo and hydroxy derivatives.[173] Acetals and cyclic and acyclic ethers are also oxidised by dioxiranes to give the corresponding carbonyl compounds,[174] whereas aldehydes are converted into the corresponding carboxylic acids;[1] oxidation of substituted benzaldehydes by the dioxirane **1a** follows a radical mechanism.[119] Ethylene ketals undergo oxidative cleavage.[174]



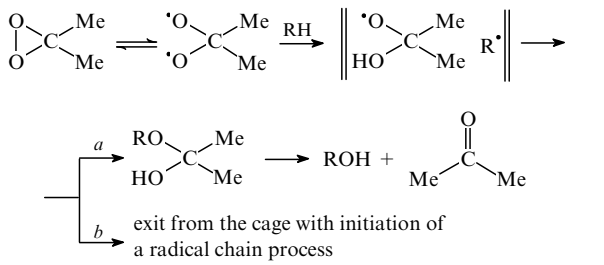
The reaction of diphenylmethane with dimethyldioxirane affords Ph_2CO (92%). In this case, the methylene carbon atom, which is absolutely inert under other circumstances, can be oxidised because the CH_2 unit is activated by the two phenyl groups.[175] Phenylcyclopropanes and halophenyl-substituted cyclopropanes do not react with the dioxirane **1a**,[176] whereas bicyclo[4.1.0]heptane and *exo*-9-bromobicyclo[6.1.0]nonane are converted into the corresponding ketones.[176]

Dioxiranes have also been used to oxidise vegetable oil components,[177] caffeine and purine nucleosides.[178]

At present, two possible mechanisms for the reaction of dioxiranes with alkanes are being discussed in the literature, namely, insertion of an oxygen atom into the C–H bond of the substrate (by analogy with the oxenoid mechanism, proposed previously for the oxidation by ozone [179]) [reaction (8)] and a free-radical mechanism [reaction (9)].



(8)



(9)

In the former case, oxidation of the substrate by a dioxirane passes through the formation of transition state **A** [reaction (8)], while in the latter case, dioxirane first undergoes homolytic cleavage at the O – O bond, the dioxirane biradical abstracts an H atom from the substrate and then the radicals either undergo intracage recombination [reaction (9), pathway (*a*)] to give the oxidation products or leave the cage and initiate a radical chain process [reaction (9), pathway (*b*)], or both pathways occur in parallel.

The main argument favouring the former mechanism is the high selectivity of a large number of reactions of oxidation of saturated hydrocarbons by dioxiranes, which could hardly be expected in the case of a radical chain mechanism. The selectivity of the reactions of the dioxiranes **1a** and **1b** with *cis*- and *trans*-1,2-dimethylcyclohexanes,[111, 145] 2-norborneols [162] and with the *para*-substituted isopropylbenzenes **23** [121, 145, 147, 148] have already been noted above. The oxidation of 3-methyltetrahydropyran is equally selective:[174] an oxygen molecule is inserted exclusively at the two α-positions, whereas in the case of a radical mechanism, the β-positions of the substrate would also undergo oxidation. Oxidation of *R*-(–)-2-phenylbutane **20** occurs with retention of the configuration [reaction (7)], whereas in the case of a radical chain process, at least partial racemisation would be observed. The relatively large negative values of activation entropy [146] (Table 3) provide more evidence for the formation of an ordered transition state of type **A** [reaction (8)].

Table 3. Rate constants (k_2 /litre mol^{-1} s^{-1}) and activation parameters for the oxidation (E_a /kcal mol^{-1}; $\Delta S^{\neq}$ /cal mol^{-1} K^{-1}; $\Delta G^{\neq}$ /kcal mol^{-1}) of 2-phenylbutane with the dioxirane **1b**.[146]

Solvent	T/ °C	$k_2 \times 10^2$	E_a [a]	log$A$	$\Delta S^{\neq}$ [a]	$\Delta G^{\neq}$
CH_2Cl_2	–15.0	2.83				
	0.0	7.34	9.7±0.2	6.6±0.2	–30±2	17.4
	9.9	15.10				
$CF_3C(O)Me$	–19.8	0.55				
	0.0	2.58	11.3±0.2	7.4±0.2	–26±2	17.9
	9.7	5.82				

[a] Found from the plot for log k_2 *vs* $1/T$ (in K).

The formation of transition state **A** is supported by the data [180] on the reaction of dimethyldioxirane **1a** with *cis*-1,2-dimethylcyclohexane in various solvents (Table 4). The reaction is facilitated by proton-donating solvents, which stabilise the spiro transition state.

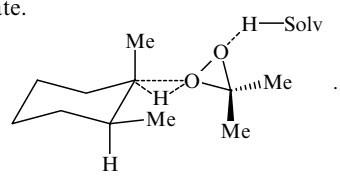


Table 4. Second-order rate constants for the reaction of dimethyldioxirane (**1a**) with *cis*-1,2-dimethylcyclohexane.[180]

Solvent	$k_2 \times 10^3$/ litre mol^{-1} s^{-1}	Relative reactivity
MeC(O)Me	1.37±0.03	1.00
MeC(O)Et	1.29±0.01	0.94
MeC(O)OEt	1.02±0.02	0.74
CH_2Cl_2	3.08±0.06	2.25
$CHCl_3$	4.44±0.13	3.24
$CDCl_3$	4.05±0.04	2.96

Note. The reaction was carried out in a solvent–acetone mixture (1 : 1) at 0 °C.

Kinetic data provide additional evidence supporting the 'insertion' mechanism; reactions described in numerous studies [8, 37–39, 121, 145–147, 151, 162, 180] obey second-order kinetics (first-order kinetics with respect to each reactant). The fairly moderate primary kinetic isotope effect observed in the oxidation of cyclohexane-d_{12} ($k_H/k_D \approx 2$) [121] also points to a molecular mechanism of the reaction. In those cases where the reaction rate is limited by radical abstraction of a hydrogen atom from an sp^3-hybridised carbon atom, the primary isotope effect increases substantially and can be greater than 10.[181, 182]

Comparison of the relative reactivity of the dioxiranes **1a** and **1b** with respect to cumene and ethylbenzene [121, 145] with the reactivity of the $Bu^tO^{\bullet}$ radical showed that dioxiranes are more selective; this also provides evidence for reaction (8). Finally, the mechanism of insertion is in good agreement with the results of theoretical calculations.[183]

Despite all the above facts, which attest to the insertion mechanism, the radical reaction mechanism [reaction (9)] has been still considered in a number of recent publications.[34–36, 184–190] An early publication that considered the radical character of the interaction of the dioxirane **1a** with alkanes and appeared in 1989 [119] dealt with the influence of O_2 on the products formed upon oxidation by dimethyldioxirane **1a** of a series of substituted benzaldehydes. The radical mechanism has been considered as a possible mechanism of oxidation of *para*-substituted α-methylbenzyl alcohols.[163]

Later, the Minisci's research group [34] has obtained data on the strong influence of oxygen and inhibitors on the rate and the products of oxidation of a number of alkanes by the dioxirane **1a**. Thus it was found that the degree of conversion of alkanes in oxygen-free systems is much lower than that attained under ambient conditions, the corresponding alkyl acetates being formed as the major reaction products. Meanwhile, in the presence of O_2, the formation of acetates is largely suppressed. Trapping by TEMPO made it possible to detect the corresponding adducts with alkyl radicals. However, it was noted that TEMPO could induce decomposition of the dioxirane. This assumption has later been confirmed in another study.[124]

When the reaction of the dioxirane **1a** with cyclohexane and adamantane was carried out in the presence of chinaldine, adducts of the trap with alkyl radicals were isolated.[184] The reactions of alkanes and adamantane with the dioxirane **1a** in the presence of $CBrCl_3$ resulted in a set of halo-containing products, their ratio being dependent on the **1a** : $CBrCl_3$ ratio.[35] These and other experimental facts led Minisci *et al* [34, 35, 184–186] to the conclusion that in the presence of alkanes, the compound **1a** undergoes radical chain decomposition induced by the alkyl radicals that have left the cage according to pathway *b* [reaction (9)]. The radical chain model has later been extended to reactions of dimethyldioxirane **1a** with esters and aldehydes.[184]

The high selectivity of the oxidation of alkanes by dioxiranes was attributed to the unusual selectivity of the dioxirane biradical, compared with other alkoxy radicals; this biradical can selectively abstract an H atom from the substrate, which leads subsequently to the formation of the reaction products [reaction (9), pathway *a*]. Meanwhile, oxygen present in the system reacts with the radicals having left the cage [reaction (9), pathway *b*] and thus prevents the development of a radical chain process.[34]

Analysis of the kinetic features of the oxidation of cumene by dimethyldioxirane **1a** and the products and the thermochemistry of the process also attest in favour of the radical character of the reaction.[36] An indirect proof of the formation of radicals is the slight chemiluminescence (obviously, caused by recombination of peroxyl radicals [191]) in the visible region of the spectrum, which accompanies the reaction in question when it is carried out in the presence of oxygen.[187] According to the radical mechanism being discussed, chain decomposition of the dioxirane **1a** (in the absence of O_2) is responsible for its 'idle' consumption; therefore, the yields of the products of oxidation of cumene based on the converted dioxirane are relatively low.[36] A radical mechanism has also been proposed for reactions of the dioxirane **1a** with isopentane [189] and adamantane.[190]

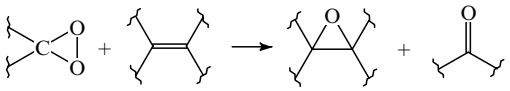
However, it can be easily seen that a radical chain mechanism for the reactions of dioxiranes with saturated hydrocarbons is at variance with the kinetic curves and with the high selectivity of oxidation reactions, which can be perfectly explained in terms of the insertion mechanism [reaction (8)]. These contradictions were partially eliminated in the study by Curci *et al.*,[37] which dealt with the oxidation of adamantane **24** by the dioxirane **1a** under various conditions. When the **1a** : **24** molar ratio was ~1 : 1.2, the oxidation gave an alcohol, 1-AdOH (91.5%), and a diol, 1,3-$Ad(OH)_2$ (4.5%). However, the reaction in the presence of CCl_3Br (*i.e.*, under the conditions used in the above-mentioned study by Minisci *et al.*[35]) was appreciably less selective and yielded a series of side products: 1-AdBr (42.3%), 1-AdCl (9.2%), 2-AdBr (10.5%), 2-AdCl (2.5%), 2-AdOH (2.0%), adamantanone (< 0.5%), *etc.*[37] The reaction kinetics, which corresponded to the simple second order without CCl_3Br (both in air and under an atmosphere of N_2), became more complex in the presence of this additive. It was also found that the addition of CCl_3Br induces rapid radical decomposition of the dioxirane **1a**.[37]

Curci, Adam, *et al.*[37–39] suggested that, when there are no factors able to induce decomposition of dioxirane (various admixtures, for example, metal ions, irradiation with light, *etc.*) and when there is no O_2, the radical chain mechanism is not involved in the oxidation of alkanes. The influence of drying agents (*e.g.*, $MgSO_4$) and impurities introduced together with drying agents can also be regarded as destabilising factors of this type. Other factors that should also be taken into account include temperature (it is reasonable to expect that at higher temperatures, the proportion of radical processes would increase and thus the process selectivity would decrease) and the nature of the substrate being oxidised (structural features, C–H bond strength, *etc.*).

An interesting view on the mechanism of reactions of dioxiranes with saturated hydrocarbons has been expressed by Asensio *et al.*[192] A thorough study of the primary kinetic isotope effect and the products of the reaction of the dioxirane **1a** with cyclohexane and methylcyclohexane at various reaction conditions, both in solution (0 °C, Ar atmosphere) and in the gas phase (25 °C) showed that the radical chain process actually does contribute to the oxidation of cyclohexane and methylcyclohexane under experimental conditions but the major reaction products — cyclohexanone (in the case of cyclohexane) and the corresponding alcohol (in the case of methylcyclohexane) — are formed by the insertion mechanism.[192] The researchers suggested that the formation of free radicals can be due to a change in the electronic configuration of dioxirane [namely, transition into the triplet $(\pi, \pi^*)^3$ state with the properties of a biradical] induced by interaction with an alkane. Depending on the energy and the route of this interaction, the process follows either a radical chain mechanism (β-cleavage of the biradical to give methyl radicals) or an insertion mechanism [reaction (8)].[192]

2. Oxidation of unsaturated compounds

Epoxidation of compounds containing double bonds is the best studied oxidative reaction of dioxiranes, which is often used for synthetic purposes.



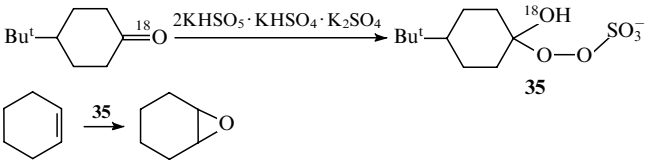
These reactions usually proceed at high rates, give products in good yields and are stereospecific. Yet another advantage of these reactions is that the possibility of conducting them under mild conditions (low temperatures, neutral medium) is combined with the possibility of isolating unstable epoxides; this can be seen taking the synthesis of pH-sensitive oxaspiropentanes from the corresponding methylenecyclopropanes as an example.[193] Dioxiranes efficiently epoxidise alkenes containing electron-donating

substituents,[104, 107, 194–196] which obviously makes them better epoxidising agents compared to other peroxides because dioxiranes are more reactive; this allows the synthesis of relatively labile epoxides. The fact that dioxiranes are able to oxidise electron-unsaturated alkenes is equally significant.[103, 104, 197–199] Although these reactions are usually rather slow, the use of excess dioxirane makes it possible to attain high yields of epoxides.

Epoxidation can be carried out both using isolated dioxiranes and *in situ*.[103, 104, 106 107, 200–205] In the latter case, the pH of the medium should be strictly controlled (7.3–7.5). The procedures using isolated dioxiranes are not faced with this problem. In some cases, phase transfer catalysts are used (for example, for water-insoluble substrates). In this respect, the *in situ* procedure with the use of Caro's acid derivatives (peroxomonosulfates) seems quite promising.[206] In this procedure, dioxiranes are generated in a homogeneous organic medium, which substantially facilitates the oxidation. An advantage of the *in situ* method is that ketone is virtually not consumed in the reaction (only the oxone is consumed) and can be quantitatively recovered after its completion.

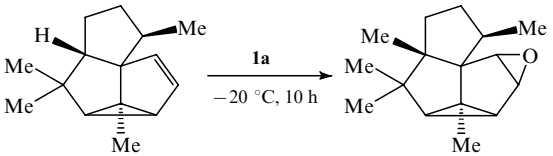
The *in situ* reactions in which the corresponding optically active ketones are used as the precursors of dioxiranes present considerable interest.[107, 203–205] Thus the use of (+)-3-(trifluoroacetyl)camphor or *R*-(+)- and *S*-(−)-4,4,4-trifluoro-3-methoxy-3-phenylbutan-2-one as the initial ketones allowed asymmetric epoxidation of prochiral alkenes (*trans*-β-methylstyrene, *trans*-oct-2-ene, *cis*-2-methyloctadec-7-ene) with optical yields of 12%–20%.[203] Enantioselective epoxidation of *trans*-stilbene and its 4,4′-dialkyl-substituted homologues catalysed by chiral ketones in the presence of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) at ~20 °C affords the corresponding epoxides (yields 90%–95%) with 75%–93% enantiomeric purity.[204]

Regarding the *in situ* oxidation, it is noteworthy that, based on the experiments with ^{18}O isotope labelling, it has been suggested that the dioxirane intermediate is not responsible for the *in situ* epoxidation of alkenes.[207] Thus in the epoxidation of cyclohexene, it is not dioxirane that acts as the main oxidation agent but rather the product of addition of the $HOOSO_3^-$ anion to the carbonyl group of the transferring ketone — compound **35** (corresponding to intermediate **A** in Scheme 2).[207]

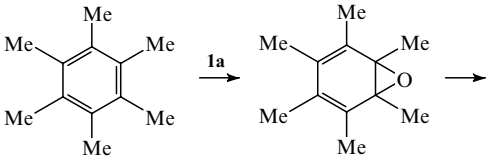


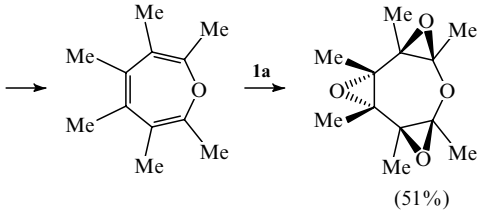
The reactions of dioxiranes (both *in situ* and in a pure state) with *cis*- and *trans*-alkenes are stereoselective: *cis*- and *trans*-alkenes are converted into *cis*- and *trans*-epoxides, respectively (the *cis*-compounds are more reactive).[103, 104, 107, 195, 196, 208]

Treatment of strained polycyclic alkenes with the dioxirane **1a** resulted in the synthesis of the corresponding epoxides.[209]



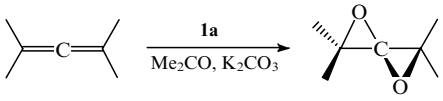
Oxidation of hexamethylbenzene by the dioxirane **1a** gives hexamethylbenzene polyoxides *via* the intermediate formation of 2,3,4,5,6,7-hexamethyloxepine.[210]





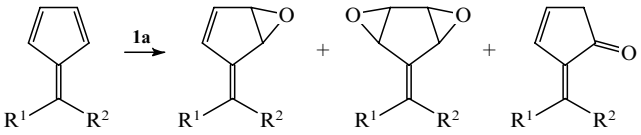
exo,*exo*,*exo*-3,6,9-Tris(4-methylphenylsulfonyloxymethyl)-*cis*,*cis*-cyclonona-1,4,7-triene reacts with this dioxirane in a similar way.[211]

The dioxirane **1a** oxidises allenes and their derivatives (allene alcohols and acids) to give the corresponding dioxides.[212–216]



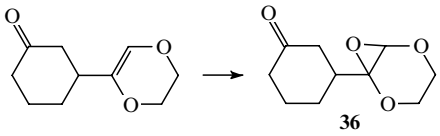
On treatment with the dioxirane **1a**, (*E*)- and (*Z*)-arylideneindolones give the corresponding spiro epoxides in 70%–90% yields (the process is fully diastereoselective).[217]

The reactions of 6,6-disubstituted pentafulvenes, containing conjugated double bonds with different reactivities, with an excess of the dioxirane **1a** afford endocyclic diepoxides in good yields. When the reactants are taken in stoichiometric amounts, a mixture of mono- and diepoxides is formed[218] (the exocyclic double bond remains intact, pointing to an electrophilic nature of **1a** in the oxidation).

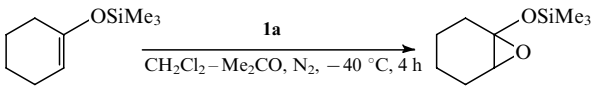


Dioxiranes are able to oxidise allyl alcohols,[106] alkenyl hydroperoxides,[172] vinylsilanes[219] and unsaturated ketones, acids and esters[220, 221] to give the corresponding epoxy derivatives in good yields.

Oxidation of 4-dioxenylcyclohexanone gives rise to epoxide **36**.[222]



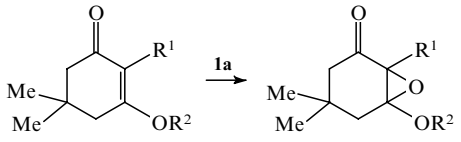
Oxidation of silyl ethers of enols by peroxides, resulting in the formation of α-hydroxy ketones, has been suggested to occur *via* intermediate epoxide.[223] This type of epoxide also proved to be produced from silyl ether, phosphates and esters of enols as well as from γ,δ-unsaturated 5- and 6-membered lactones on treatment with the dioxirane **1a**. These compounds can be isolated in a pure state.[224]



High yields (92%–97%) of spiro oxiranes have also been detected in the oxidation of enol ethers, for example alkoxy(aryl)methylideneadamantanes and methoxy(2-naphthyl)-methylidene-2-bornane by the dioxirane **1b**.[225] Note for comparison that synthesis of epoxy esters and strained oxaspiroalkanes involving peroxy acids often does not lead to acceptable results, because the oxiranes formed in the reaction rearrange in the presence of acids to give α-alkoxy or α-hydroxy ketones.

The ability of the dioxiranes **1a** and **1b** to epoxidise electron-unsaturated alkenes can be illustrated by the oxidation of 4-substituted (*E*)-ethyl cinnamates by the dioxirane **1a**.[198] Enol ethers of

β-diketone, which are relatively inert, can also be quantitatively epoxidised by the dioxirane **1a**.[199]



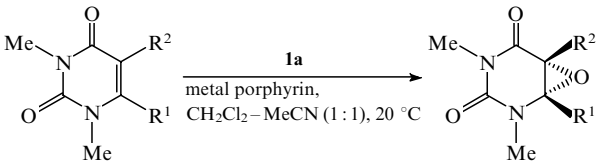
R^1 = H, Me; R^2 = Et, Bu, Ph.

The corresponding epoxides are also formed in the oxidation of enol phosphates,[226] γ-methylene-γ-butyrolactones[227] and acyl- and allylferrocenes.[228]

Epoxidation of primary and secondary alkenylammonium salts by the dioxiranes **1a** and **1b** gives rise to epoxy derivatives; on treatment with sodium carbonate, they are readily converted into epoxyalkylamines, formed in good yields.[229] The epoxidation rate is lower than that in the case of epoxidation of simple alkenes because the double bonds are deactivated due to the ammonium groups.

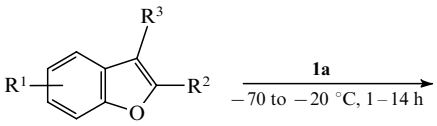
Adam *et al.*[230] were able to detect the low-temperature NMR signals of epoxides of *cis*- and *trans*-(2-methyloxiranyl)benzamide, which result from oxidation of (*E*)- and (*Z*)-*N*-propenylbenzamides by the dioxirane **1a**.

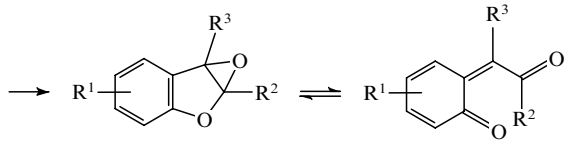
Examples of catalytic epoxidation of alkenes by dioxiranes have been reported in several studies.[231–233] Thus epoxidation of 2,2-dimethyl-2*H*-chromenes by the dioxirane **1a** in the presence of chiral Mn(III)(salen) complexes (Jacobsen catalysts) occurs enantioselectively. Selective synthesis of epoxides of uracil derivatives (important intermediates in oxidative transformations of DNA) catalysed by metal porphyrins has been described.[233] (The attempt to prepare uracil epoxides without a catalyst using the dioxirane **1a** as the oxidant was less successful; the yields of the corresponding epoxides were low and side products formed[234]). The reaction was carried out in CH_2Cl_2 – MeCN (1 : 1) at 20 °C in the presence of imidazole.



Other dioxiranes also possess high oxidative potentials.[1,81,82,117,235] Thus ethylmethyldioxirane **1m** has been used to epoxidise natural triglycerides in the butan-2-one – water two-phase system in the presence of the 18-crown-6 ether,[235] while difluorodioxirane **1k** has been employed to epoxidise fluorinated alkenes $CF_3CF = CF_2$ and $F_2C = CFCl$ (the yields of epoxides are > 95%).[82]

Special mention should be made of those studies that are valuable not only for synthetic purposes but also from the medical or biological viewpoint. For example, this is true for several works[236–245] dealing with epoxidation of furans by dioxiranes. Benzofurans are known to be toxic for animals and humans. Their toxicity may be due to the presence of labile epoxides, resulting from oxidation of the furan ring.[236,246,247] However, benzofuran epoxides had not been detected even at low temperatures. This became possible only using the dioxirane **1a**.[236–243] This reagent was employed to prepare epoxides of substituted benzofurans, occurring in equilibrium with the corresponding quinonemethides.

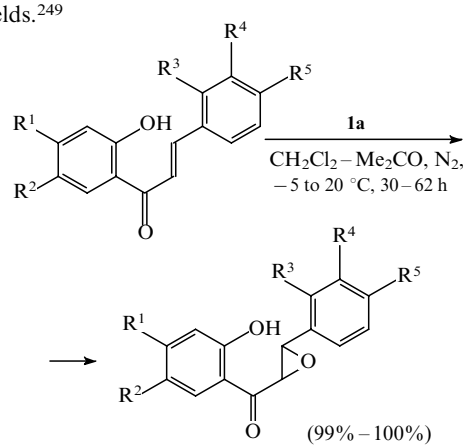




R^1 = H, Me, OMe, Cl, MeCO; R^2 = H, Me, CH_2OH, CH(OMe)Ph, CO_2Et; R^3 = H, Me, Bu^t, $C_6H_3R^4R^5$-3,4 (R^4 = H, NO_2; R^5 = H, MeO).

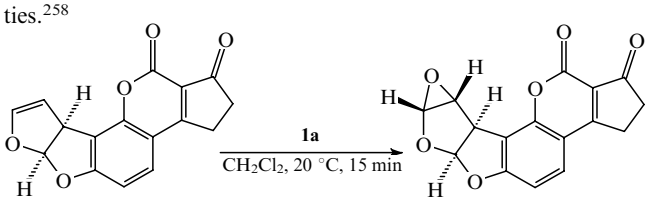
Using the dioxirane **1a**, regio- and stereoselective oxidation of the C(3) = C(4) enol bonds in the molecules of biologically active triterpenes containing a norquinonemethide fragment (*e.g.*, pristimerin, tingenone) was attained.[248]

Oxidation of steroids, flavones and chalcones by dioxiranes is equally important.[249–257] Chalcone epoxides are significant building blocks in organic synthesis; they play an important role in the biosynthesis of many flavonoid systems. Oxidation of hydroxychalcones by the dioxirane **1a** resulted in the formation of epoxide products, unstable in acidic or alkaline media, in high yields.[249]



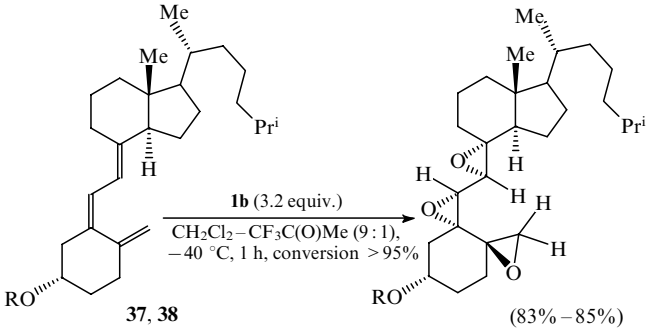
R^1	R^2	R^3	R^4	R^5
H	Cl	H	H	H
H	H	H	H	Cl
H	H	MeO	H	H
H	H	H	MeO	H
Me	H	H	H	H
H	Me	H	H	MeO
H	Cl	H	H	MeO

Epoxidation reaction has been successfully used to prepare the 8,9-epoxide of the aflatoxin B_1, noted for its carcinogenic properties.[258]



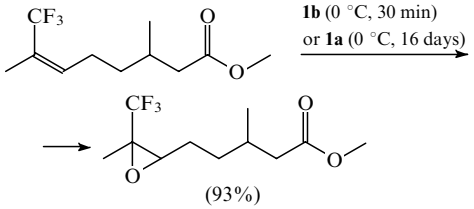
The reactions of the dioxiranes **1a** and **1b** with vitamin D_3 and its 3-*O*-acylated derivatives were reported to be highly selective.[259] The reaction of 3β-acetyl- (**37**) and 3β-(*p*-bromobenzoyl)-derivatives (**38**) of vitamin D_3 with methyl(trifluoromethyl)dioxirane **1b** gives rise to the corresponding (*R*,*R*,*R*)-triepoxides.

On treatment with the same dioxirane, vitamin D_2 and its 3β-*O*-acetyl-derivative are converted into the corresponding (*R*,*R*,*R*,*R*)-tetraepoxides.[260]

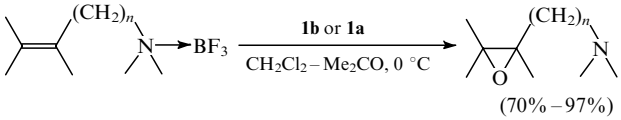


R = Ac (**37**), *p*-BrC_6H_4CO (**38**).

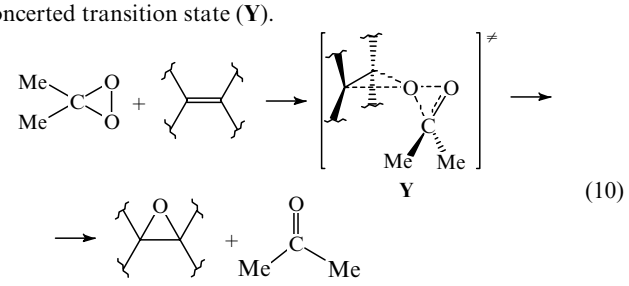
Mention should be made of interesting studies [261, 262] in which dioxiranes have been used to synthesise epoxy-derivatives of insect juvenile hormones, which play an important role in the growth and development of insects. An example of epoxidation of a compound containing a CF_3 group at a double-bond carbon atom has been reported.[262]



Epoxidation of aminoalkenes is used to prepare indole alkaloids. However, epoxidation of this type of substrates by traditional reagents is hampered by the predominant oxidation of the nitrogen atom. Only recently,[263] were epoxides of several tertiary amines containing alkenyl groups synthesised chemoselectively using dioxiranes in the presence of $BF_3 \cdot Et_2O$.



The reactions of dioxiranes with alkenes (Table 5) is described by a second-order equation [39, 116, 195, 196, 198, 264, 265] (*cis*-isomers react approximately 10 times faster than *trans*-isomers). Based on experimental data, a reaction mechanism has been proposed,[196] which includes a stage of formation of a spiro-type concerted transition state (**Y**).

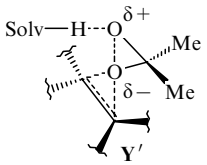


(10)

This mechanism is in good agreement with the results obtained by Murray and Gu [264] concerning the influence of solvents on the rates of epoxidation of *trans*-ethyl cinnamate and cyclohexene; analysis of the kinetic data in terms of the Kamlet – Taft equation, which takes account of the ability of a solvent to act as a hydrogen bond donor (HBD) or acceptor (HBA), showed that HBD solvents increase the rate of epoxidation, whereas HBA solvents retard this process.[264] Transition state **Y′**, which is similar to **Y** but takes into account the solvent effect on the reaction rate, explains well the characteristic features observed.

Table 5. Second-order rate constants for epoxidation of di- and monosubstituted alkenes by the dioxirane **1a** in dry acetone (according to Ref. 195).

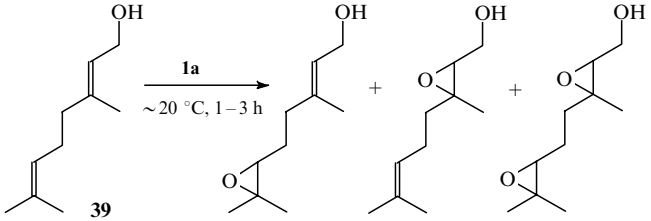
Alkene	$k_2 \times 10^2$/ litre mol^{-1} s^{-1}	Relative reactivity
cis-Hex-3-ene	47±3	8.3
trans-Hex-3-ene	5.7±0.4	1.0
cis-4,4-Dimethylpent-2-ene	33±2	5.8
trans-4,4-Dimethylpent-2-ene	2.3±0.1	0.4
cis-2,5-Dimethylhex-3-ene	39±2	6.8
trans-2,5-Dimethylhex-3-ene	2±1	0.4
trans-2,2,5,5-Tetramethylhex-3-ene	0.024±0.004	0.004
Cyclohexene	48±2	8.4
cis-1-Phenylpropene	18±2	3.2
trans-1-Phenylpropene	29±2	5.1
cis-Stilbene	4.0±0.1	0.70
trans-Stilbene	4.3±0.2	0.75
Indene	22±1	3.9
4-Methoxystyrene	57±3	10.0
4-Methylstyrene	25±1	4.4
Styrene	13±1	2.3
4-Bromostyrene	8.9±0.3	1.6
3-Nitrostyrene	3.0±0.3	0.53
3,3-Dimethylbut-1-ene	3.3±0.1	0.58
3-Methylbut-1-en-3-ol	1.6±0.2	0.28



In fact, HBD solvents (MeOH, $CDCl_3$, AcOH) stabilise the negative charge on the oxygen atom involved in H-bonding with a solvent molecule and thus facilitate epoxidation. Conversely, HBA solvents destabilise the transition state, which decelerates the reaction. This assumption accounts for the fact that addition of water (which can be regarded as an HBD solvent) increases the epoxidation rate.[195] The relatively large negative values of the entropy factor $\Delta S^{\neq}$ also support the assumed formation of an ordered spiro transition state.[264]

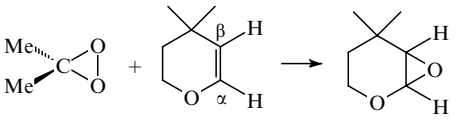
The data obtained by Messeguer *et al.*,[116] who studied the influence of solvents on the epoxidation of *cis*-stilbene by more concentrated solutions of the dioxirane **1a** (see Section II), are in good agreement with the results of Murray and Gu [264] with the only difference that in the former case,[116] the effect was more pronounced due to the use of acetone-free solutions of **1a**.

The solvent effect, like the influence of substituents, is manifested not only as a change in the reaction rate but also as a change in the diastereoselectivity and regioselectivity of epoxidation.[266 – 268] It was shown [266, 267] that diastereoselectivity of epoxidation of substituted cyclohexenes by the dioxirane **1a** is determined by the substrate structure and the solvent, which includes steric effects, dipole – dipole interactions, effects of hydrogen bonding and other factors. A similar solvent effect is involved in the epoxidation of acyclic allyl alcohols,[268] in particular, geraniol **39**.



In a polar medium, MeOH – Me_2CO (9 : 1), the ratio of the 6,7- and 3,2-monoepoxides is 88 : 12, whereas in a less polar system, CCl_4 – Me_2CO (9 : 1), it is equal to 51 : 49.[268] In fact, the Δ^6 double bond in the alcohol **39** is more nucleophilic than the Δ^2 bond, deactivated by the OH group; hence, it is the Δ^6 bond that will be attacked predominantly by dioxirane. Methanol stabilises the transition state due to the formation of a hydrogen bond, so that the contribution of the geraniol OH group to the stabilisation of the transition state is minimised.[268] Conversely, in non-polar CCl_4, the external stabilisation is much less pronounced and the transition state is largely stabilised by the OH group belonging to the alcohol **39** molecule, resulting in a higher yield of the 2,3-epoxides.[268]

An interesting situation is observed when 4,4-dimethyl-2,3-dihydro-γ-pyran **40** is oxidised by the dioxirane **1a**.[269]

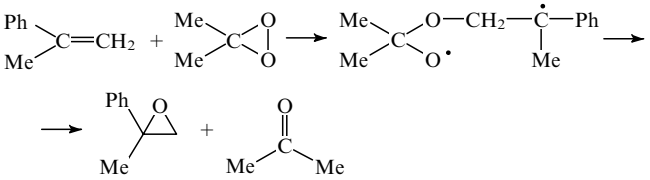


40

Measurements of the secondary kinetic isotope effect showed that in the transition state *en route* to the epoxide, the degree of rehybridisation of the β-carbon atom is higher than that of C_α. Hence, this reaction does not proceed *via* a symmetrical transition state but occurs as a non-synchronous concerted process.[269] This result cannot be extended to simple alkenes in which the electron densities at the C_α and C_β atoms are identical. In fact, the experimental values for the α- and β-isotope effects found for the reactions of **1a** with 3-methyl-1-phenylbut-2-ene and 2,2,7,7-tetramethyl-*cis*-oct-4-ene and their deuterated analogues support the formation of a concerted transition state of the spiro type.[270]

Study of the epoxidation kinetics also confirms the electrophilic mechanism of the reaction: Hammett correlations for a series of substituted styrenes[195] and 4-substituted (*E*)-ethyl cinnamates[198] give the values $\rho^+ = -0.9$ and -1.153, respectively. Study of the kinetics of epoxidation of chalcones (anhydrous acetone, 30 °C) showed that electron-donating substituents at 4 and 4′-positions accelerate the reaction (for 4- and 4′-substituted chalcones, $\rho^+ = -1.03$ and -0.182, respectively).[265]

As noted above, experimental results point to a molecular mechanism of the epoxidation of alkenes by dioxiranes [reaction (10)]. However, arguments for a free radical mechanism of epoxidation have also been reported.[185] Thus the oxidation of α-methylstyrene by the dioxirane **1a**, in addition to the epoxide (35%) and α-phenylpropionaldehyde (51%), resulting from its rearrangement, gave the allyl alcohol $PhC(CH_2OH) = CH_2$ (6%) and the corresponding aldehyde $PhC(CHO) = CH_2$ (5%). It was suggested[185] that alkenes can induce homolysis of dimethyldioxirane **1a** and the formation of epoxides can be explained in terms of a radical mechanism.



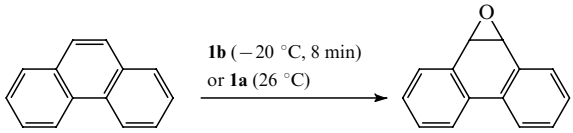
These data, which contradict the molecular mechanism of the reaction, have been specially considered in the study by Adam, Curci, *et al.*[39] The results obtained by these researchers[39] indicated that the reactions of alkenes with dioxiranes involve no radical processes. In particular, the reaction of the dioxirane **1a** with α-methylstyrene obeys second-order kinetics both under ordinary conditions and under an inert atmosphere (N_2), the corresponding epoxide being the only reaction product (neither allyl alcohol nor the aldehyde were detected even under conditions most favourable for radical chain processes, *viz.*, in the presence of $CBrCl_3$ at 56 °C). Investigation of epoxidation of *trans*-cyclooctene and 2-vinylcyclopropane also supported the hypothesis that no radical chain processes are involved.[39]

These examples indicate once again that, in all probability, in the absence of factors that could induce a radical chain process, oxidation of alkanes and alkenes by dioxiranes does not include radical pathways of transformation.[37–39]

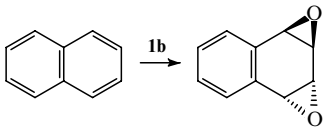
3. Oxidation of polyaromatic hydrocarbons

Study of the chemical transformations of PAH on treatment with dioxiranes is an exceptionally important problem, if for no other reason than that many PAH are hazardous carcinogens. The mutagenic and carcinogenic action of PAH is preceded by a metabolic activation process,[271] comprising a complex sequence of oxidative transformations, unstable arene oxides being the most significant intermediates in these processes. These important intermediates are prepared in most cases using multistage syntheses. The use of direct oxidation by classical reagents (peroxy acids, hypochlorites, *etc.*) is often restricted because many arene oxides are sensitive to acids, water or nucleophiles.

Dioxiranes are convenient reagents for oxidative functionalisation of PAH.[1,3,40,47–47,272,273] Thus the reactions of the dioxiranes **1a** and **1b** with phenanthrene in solution afford the corresponding oxide in 83% and 96% yields, respectively.[1,272]

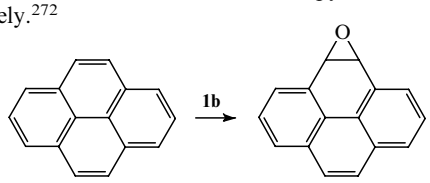


Another typical example is the reaction of the dioxirane **1b** with naphthalene, which gives *anti*-1,2:3,4-dioxide.[272]



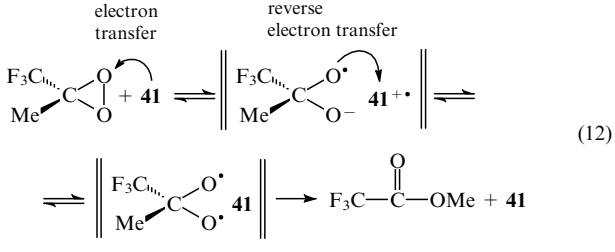
(98%)

However, the reaction with pyrene **41** occurs less effectively.[272]



41 (10%) (11)

Among the products of reaction (11), CF_3COOMe (a product of decomposition of the dioxirane **1b**, see Section III) was also detected, and the EPR spectrum of the system (−30 °C) contained a signal for the pyrene radical cation.[272] It was suggested[272] that the low yield of the oxidation products is due to the competing electron transfer reaction, giving rise to CF_3COOMe.



(12)

An essentially similar mechanism has been proposed to interpret the chemiluminescence of dioxiranes in the presence of some activating agents, which is discussed in detail in Section V.

In view of the formation of dioxiranes in gas-phase ozonisation of unsaturated hydrocarbons,[41–44] the relatively high concentrations of O_3, alkenes and PAH in the atmosphere and the carcinogenic properties of PAH, Murray *et al.*[1,3,40,46] suggested that reactions of dioxiranes with PAH might be responsible for the formation of carcinogenic compounds in the atmosphere. To verify this hypothesis, gas-phase oxidation of PAH under conditions close to the atmospheric conditions was carried out.[3,46,47] A gas stream of the dioxirane **1a** in acetone or a $Me_2CO-CH_2Cl_2$ mixture was directed at PAH supported on silica gel. Although in most cases, the yield of the resulting oxides was lower than that in the case of liquid-phase oxidation, this experiment demonstrated that dioxiranes can be involved in possible atmospheric reactions with PAH. Moreover, when PAH deposited on silica gel were oxidised by the $O_3-Me_2C{=}CMe_2$ gas mixture,[47] the reaction gave products similar to those obtained when the dioxirane **1a** is used as the oxidant (ordinary ozonolysis does not yield this type of products under these conditions).

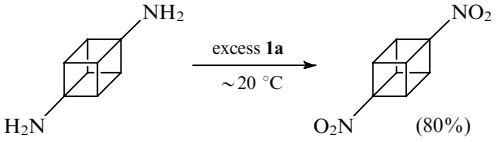
4. Oxidation of compounds containing heteroatoms

a. Nitrogen-containing compounds

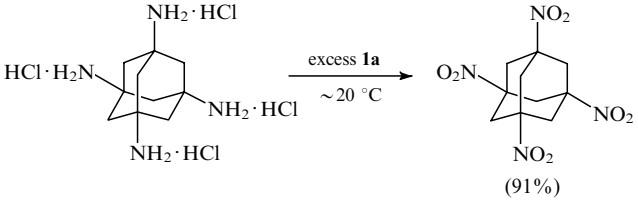
Oxidation of primary amines by dimethyldioxirane **1a** occurs rapidly (taking from several minutes to several hours) and affords the corresponding nitro compounds.[274,275]

$$RNH_2 \xrightarrow{\mathbf{1a}} RNO_2$$

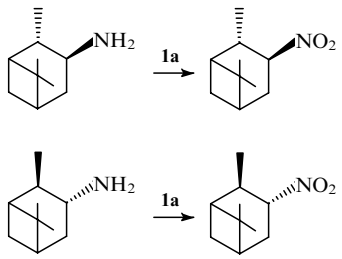
Polyamines are also converted into nitro compounds. Thus 1,4-diaminocubane reacts with **1a** to give 1,4-dinitrocubane.[275]



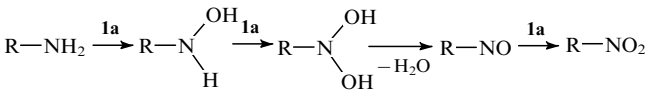
The latter compound can also be obtained by the reaction of the dioxirane **1a** with 1,4-diisocyanatocubane (however, in this case, the presence of H_2O is required).[276] Yet another typical example of oxidation of polyamines is the transformation of 1,3,5,7-tetraaminoadamantane,[275] which is extremely explosive although thermally stable.



Chiral amines are converted into the corresponding nitro compounds with retention of the configuration.[277]

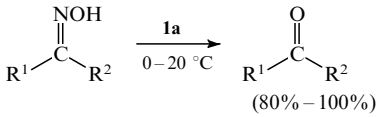


Presumably,[274] oxidation of primary amines includes several stages, hydroxylamines and nitroso compounds being formed as intermediate products; the process can be partially controlled at the stage of formation of hydroxylamine.[278]

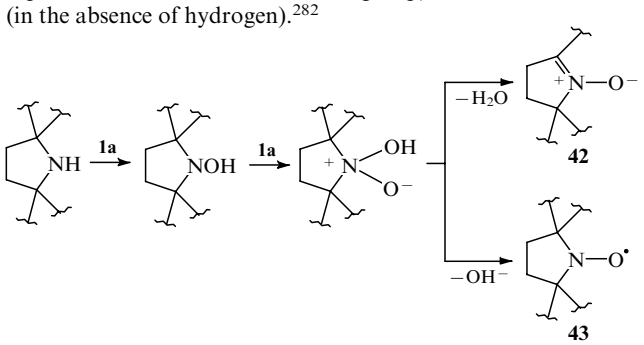


This sequence of reactions can include either insertion of oxygen into the N–H bond (similar to the insertion into C–H bonds of saturated hydrocarbons) or formation of an intermediate such as *N*-oxide followed by its rearrangement into hydroxylamine.[277]

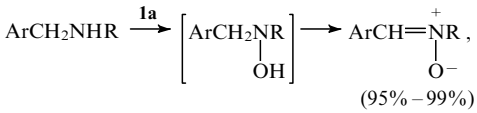
Nitro compounds are not always the only reaction products. Thus oxidation of some aliphatic primary amines by the dioxirane **1a** (either isolated or *in situ*) gives, depending on the reaction conditions, oximes, nitrosoalkanes, nitroalkanes and oxaziridines.[279] In some cases, the corresponding nitrones, arising upon oxidation of intermediate imines, can also be found among the reaction products.[279] Oxidation of ketoximes by the dioxirane **1a** gives the corresponding ketones in high yields.[280]



Secondary amines react with the dioxirane **1a** (1 : 1) to give hydroxylamines.[281] When excess dioxirane is used, the process affords either nitrone **42** (in the presence of hydrogen at the α-position in relation to the amino group) or stable nitroxide **43** (in the absence of hydrogen).[282]



A series of nitrones have been prepared by the reaction of the dioxirane **1a** with aryl-substituted secondary amines [283,284]



while oxidation of *N*-methylaniline gives rise to dinitrone.[284]

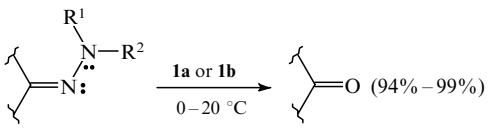
Nitroxides are formed in good yields when secondary amines are oxidised by dioxiranes generated *in situ* in the system $Me_2CO-(2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4)-CH_2Cl_2-H_2O-Bu_4NHSO_4$ (phase transfer catalyst).[285]

Tertiary amines including pyridines are oxidised by the dioxiranes **1a** and **1b** to give *N*-oxides.[3,105,263,286,287]

$$R_3N \xrightarrow{\mathbf{1a}\ (\text{or}\ \mathbf{1b})} R_3\overset{+}{N}{-}O^-$$

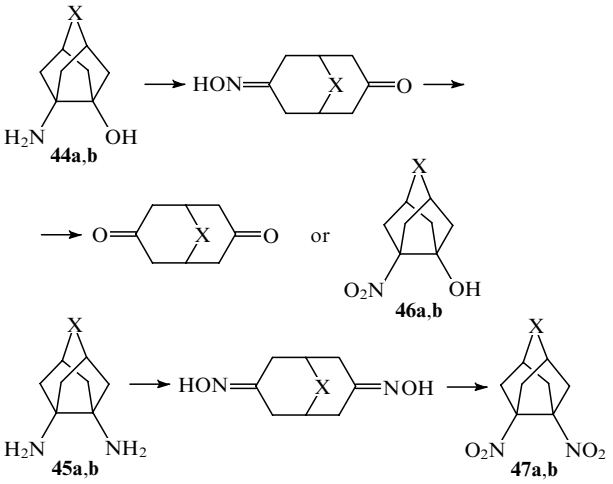
It is noteworthy that some *N*-oxides cause decomposition of dioxiranes,[3,263,286] which gives singlet oxygen [286] (see Section V).

Dioxiranes proved to be convenient reagents for the recovery of the initial ketones from derivatives of hydrazones,[288] which are often used in organic chemistry to isolate carbonyl compounds from reaction mixtures and to purify them.



Recently [289] new versions of the oxidation of amines with participation of the dioxirane **1a** have been found. They include (1) oxidative fragmentation of 2-amino alcohols **44a**,**b** or 1,2-diamines **45a**,**b** to give the corresponding mono- and dioximes of bicyclic diketones and (2) intramolecular oxidative transforma-

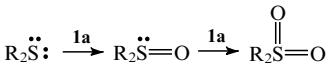
tion of the latter into tricyclic 2-nitro alcohols **46b** and 1,2-dinitro compounds **47a**,**b**.



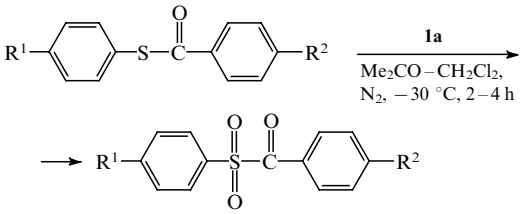
X = CH_2 (**a**), C_6H_4-*o* (**b**).

b. Sulfur- and phosphorus-containing compounds

Dioxiranes selectively oxidise sulfides to the corresponding sulfoxides (equimolar ratio of the reactants) and sulfones (excess dioxirane).



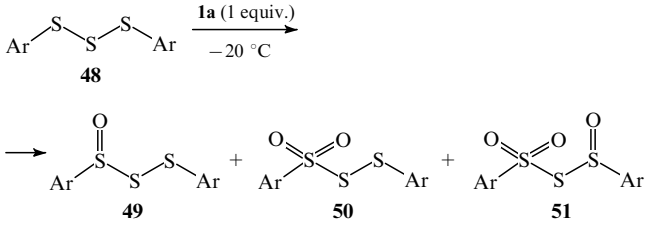
Thus thioesters are quantitatively oxidised by dimethyldioxirane **1a** to give labile α-oxo sulfones.[290]



Oxidation of (*Z*)-thioaurones, (*E*)-3-arylidene-1-thiochroman-4-ones and (*E*)-3-arylidene-1-thioflavan-4-ones by the dioxirane **1a** gives rise to the corresponding sulfones and/or sulfoxides.[291] The reaction of the dioxirane **1a**, taken in an excess, with ketene *S*,*S*-acetals, thioacetals and thioketals affords the corresponding bis(sulfones) in excellent yields.[292] When bis(sulfides) are treated with one, two or three equivalents of dimethyldioxirane, this gives monosulfoxides, bis(sulfoxides) and sulfoxide sulfones, respectively, the ratio of the products depending appreciably on the reaction temperature and the order in which the reactants are mixed.[292]

The corresponding sulfides and sulfones are formed in high yields in the chemoselective oxidation of the pentacarbonyl[amino(arylthioalkyl)carbene]chromium(0) complex by the dioxirane **1a**.[293]

Low-temperature (−20 °C) oxidation[294] of bis(*p*-methoxyphenyl)trisulfane **48** results in the formation of monooxide **49** and a small amount of 1,1-dioxide **50** and trisulfane-1,1,3-trioxide **51**.

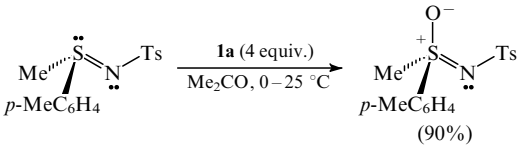


Ar = 4-$MeOC_6H_4$.

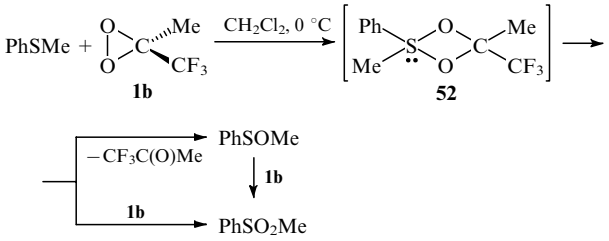
High enantiomeric yields have been attained in the oxidation of prochiral sulfides to chiral sulfoxides by dioxiranes generated *in situ*.[295]

In reactions with sulfides, dioxiranes act as electrophilic reagents; the Hammett correlations found for the oxidation of a series of methyl 4-R-phenyl sulfides to sulfoxides and oxidation of sulfoxides to sulfones gave the values $\rho^+ = -0.77$ and -0.76, respectively, the reactions of dioxiranes with sulfides being faster than those with sulfoxides.[296] Using the reaction with thianthrene 5-oxide as an electrophilicity test,[297] Adam and Golsch[298] also confirmed the electrophilic nature of the dioxirane **1a** as an oxidant.

This is indicated by the fact that the rate of oxidation of sulfylimines containing electron-donating substituents in the aromatic nucleus by the dioxirane **1a** is markedly higher than the rate of oxidation of sulfylimines with electron-withdrawing substituents.[299] It is noteworthy that the above-described method proved to be convenient for the synthesis of chiral sulfoxyimines (optical purity 80%).



When considering the mechanism of oxidation of sulfur-containing compounds, mention should be made of a study[300] dealing with the oxidation of methyl phenyl sulfide by the dioxirane **1a** and postulating the formation of a hypervalent sulfurane intermediate **52**.

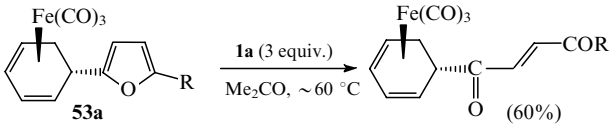


Among the few examples of oxidation of phosphorus-containing compounds by dioxiranes, the reaction of methyl(trifluoro-methyl)dioxirane **1b** with triphenylphosphine, resulting in the phosphine oxide, deserves attention; this reaction is used to determine dioxirane concentrations.

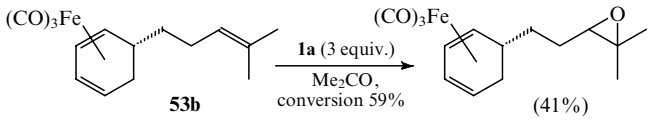
c. Oxidation of organometallic compounds

The above oxidative transformations involving dioxiranes also take place during oxidation of metal-containing compounds.[301] In the majority of cases, these reactions are highly chemoselective, because they are not accompanied by oxidative decomposition of metal complexes.

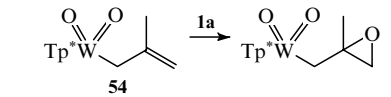
Oxidation of tricarbonyl iron complexes **53a**, containing a furylcyclohexadiene ligand is accompanied by opening of the furan ring and gives rise to the corresponding carbonyl compound.[302]

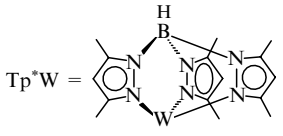


Oxidation of iron complex **53b** having a similar structure yields a 1 : 1 mixture of diastereoisomeric epoxides. The most plausible results were attained at elevated temperatures (at low temperatures, oxidative decomposition of the complex upon direct oxidation of iron occurs as a side reaction).[303]

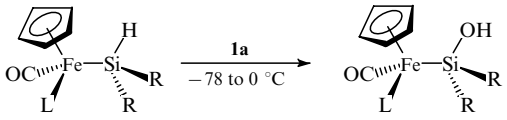


The reaction of the tungsten alkene complex with the dioxirane **1a** results in the quantitative formation of the corresponding epoxide.[304]

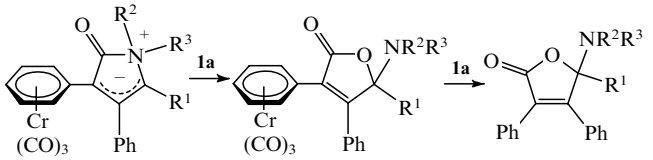




Ferrohydridosilanes react with **1a** to give the corresponding ferrosilanols.[305, 306]

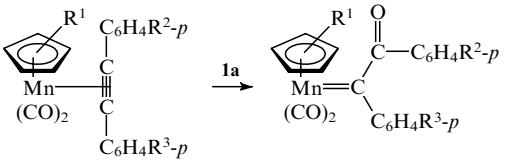


The reaction of the ylide (η^6-arene)chromiumtricarbonyl complex **55** with the dioxirane **1a** gives the corresponding lactone complex, which is converted in the metal-free lactone on further addition of the oxidant.[307]

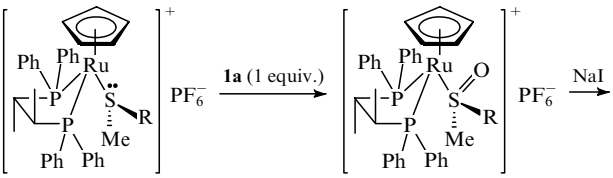


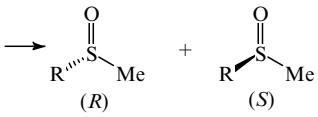
R^1 = H, Me, Ph; R^2 = R^3 = Me, R^2–R^3 = $(CH_2)_5$, R^2 = Me, R^3 = cyclo-C_3H_5.

The oxidative capacity of dioxiranes is clearly illustrated taken as an example the transformation of tolane manganese-containing complexes into α-oxocarbene complexes (apparently, this reaction proceeds *via* intermediate epoxidation of the alkyne).[308]

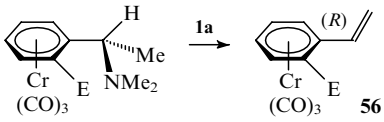


Oxidation of iron and tungsten phosphine complexes gives rise to the corresponding metal phosphine oxides.[309] Sulfur-containing metal complexes are also oxidised by dioxiranes.[310–312] Thus a new approach to the synthesis of chiral sulfoxides *via* diastereoselective oxidation by the dioxirane **1a** of a prochiral thioether incorporated in a metal complex was reported.[311, 312] A chiral sulfoxide complex of ruthenium is formed as an intermediate in this reaction. The subsequent decomposition of this complex results in the liberation of chiral sulfoxide.

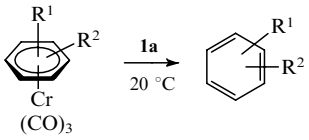




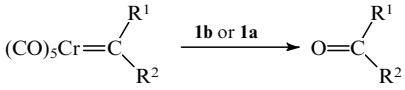
Enaniomerically pure vinyl-substituted complex **56** has been synthesised by the oxidation of chiral amino-containing (η^6-arene)chromiumtricarbonyl complex by the dioxirane **1a**.[313]



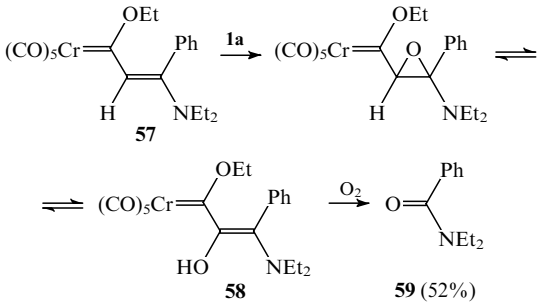
Apart from oxidation of the ligands, dioxiranes can be used for oxidative decomposition of metal complexes. Thus the organic ligands incorporated in the (η^6-arene)chromiumtricarbonyl complexes are quantitatively liberated on treatment with the dioxirane **1a**.[314]



The reaction of dioxiranes with Fischer carbene complexes follows a similar pathway.[301, 315–317]

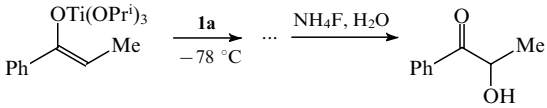


However, in the case of the Fischer complexes **57**, containing conjugated enamine fragments, the reaction loses the above-noted selectivity and yields, instead of the expected enamino ester, amide **59** *via* intermediate **58**.[317]

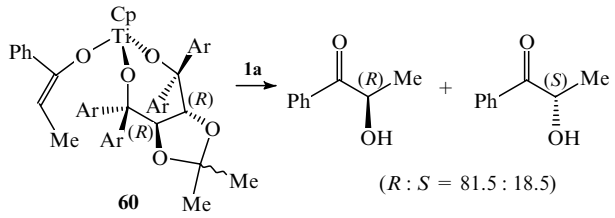


During decomplexation of (η^4-diene)irontricarbonyl and μ-(η^2-alkyne)dicobalthexacarbonyl complexes, the process of liberation of organic ligands induced by dioxirane **1a** competes with the oxidation of the unsaturated fragments present in the compounds being liberated.[318]

Lithium, sodium and titanium enolates are converted in most cases into the corresponding α-hydroxy carbonyl products.[159, 319, 320] It is of interest that the best results are achieved when the reaction is carried out at reduced temperatures.



The stereoselectivity of oxidation of chiral enolates hardly depends on the temperature and the solvent but depends on the nature of the ligands attached to the central metal atom.[320] The highest enantiomeric excess for 2-hydroxy-1-oxo-1-phenylpropane (63% *R*) is attained in the oxidation of the enolate **60** containing a chiral ligand with bulky 1-naphthyl groups, where the steric differences between the two conformers are the most pronounced.[320]

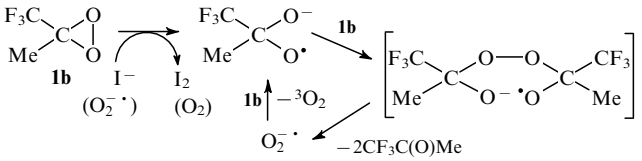


Ar is 1-naphthyl, Cp is cyclopentadienyl.

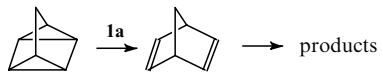
d. Other reactions of dioxiranes

Single-electron transfer reactions involving dioxiranes have been considered to a degree in Sections IV.3 and III.2 in relation to the mechanisms of oxidation of pyrene [272] and reactions of dioxiranes with nitroxides.[120, 124] A typical single-electron transfer reaction is the rapid decomposition of the dioxirane **1b** to give $CF_3C(O)Me$ and O_2 in the presence of catalytic amounts of lithium or tetrabutylammonium iodide.[321] Based on experimental data, a chain electron mechanism was proposed for the dioxirane **1a** consumption, according to which the dioxirane accepts an electron from the I^- anion being thus converted into a radical anion, which interacts with a second dioxirane molecule to give a dimeric radical anion; the latter decomposes to ketone and $O_2^{-\bullet}$. Then the $O_2^{-\bullet}$ radical anion passes an electron to a new dioxirane molecule and thus closes the catalytic cycle. Thus, the superoxide ion carries the chain, whereas the iodide anion acts as the initiator (Scheme 10).[321]

Scheme 10

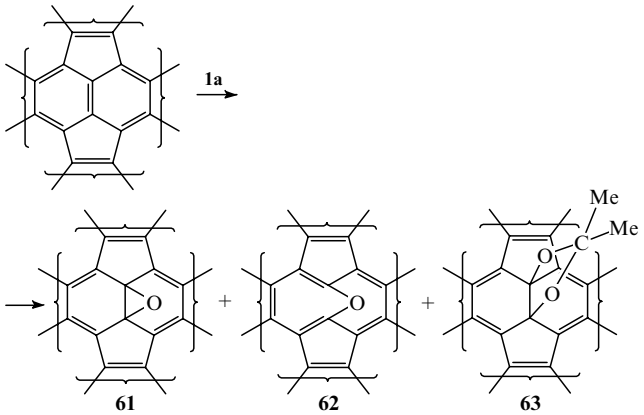


A possible mechanism of the reaction between quadricyclane and the dioxirane **1a** also implies an electron transfer.[322, 323] It is known that the dioxirane **1a**, even present in small amounts (7.4×10^{-4} mmol), is able to catalyse isomerisation of quadricyclane into norbornadiene.



In addition, it is the electron transfer that is responsible for chemiluminescence observed in the reactions of dioxiranes with PAH and Ru(II).[6, 10, 12, 15–17] Note that the capability of dioxiranes to accept an electron is in good agreement with their theoretically calculated electron affinity (2 eV).[324]

The reaction of the dioxirane **1a** with fullerene [325] is a unique example of a reaction with an organic substrate in which dioxirane

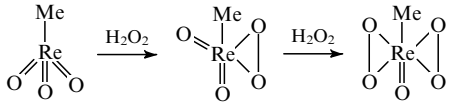


displays its biradical nature; the 1,3-dioxolane derivative **63** was detected among the products of fullerene oxidation, in addition to epoxide **61** and oxo derivative **62**.[325]

The use of the dioxirane **1a** to prepare silanol-containing polymers has been reported.[326] These polymers were synthesised by selective oxidation of SiH groups in appropriate polymer precursors.[326]

Owing to their oxidising capacity, dioxiranes have found wide use as bleaching or disinfecting reagents.[327–333]

It is worth noting in conclusion that rhenium peroxides (**64** and **65**) formed in the $MeReO_3 - H_2O_2$ system resemble dioxiranes in their structure and behave remarkably similarly to dioxiranes in the oxidation of alkenes, nitro compounds and alkanes.[334–340]



V. Chemluminescence and photochemistry of dioxiranes

Study of the dioxirane chemilumunescence started with the pioneering work by Adam and Curci, [341] who were the first to propose the possibility of CL during isomerisation (at that time, hypothetical) of dimethyldioxirane **1a** to MA [see reaction (6)]. In fact, the sum of the activation energy and enthalpy of this reaction is quite sufficient for an ester to be formed in, at least, the triplet state (Fig. 5); hence, CL is possible.[4, 5, 341] It was found that reaction (6) should also comply with other criteria necessary for the generation of electronically excited states.[341] Thus, even before alkyldioxiranes were isolated,[1] Adam and Curci [341] had discovered a new interesting chapter in their chemistry.

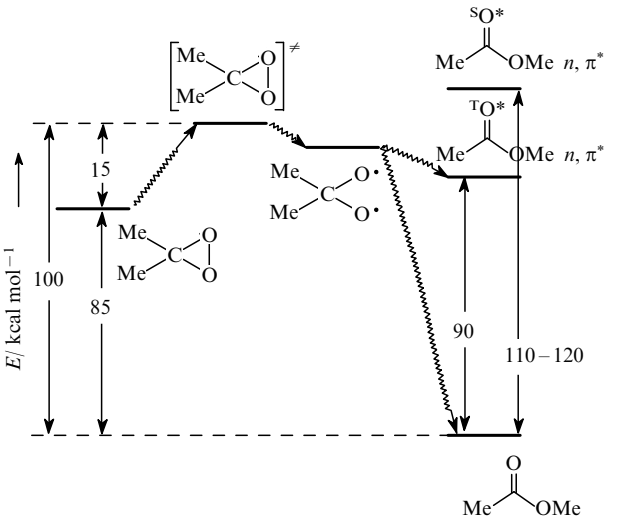
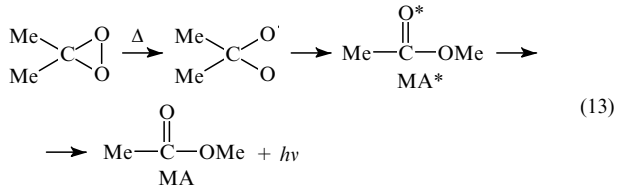


Figure 5. Diagram of the energy levels of the dioxirane **1a** in relation to the product of its decomposition, methyl acetate.

1. Non-activated chemiluminescence

Decomposition of the dioxirane **1a** in solutions under ordinary conditions is not accompanied by CL (despite the theoretical prerequisites). This can be due both to a low efficiency of emission by the electronically excited MA* in the triplet state and to efficient side 'dark' pathways of decomposition of **1a** (see Sectio-

n III). The third reason for the absence of luminescence is associated with efficient emission quenching, in particular, with the presence of traces of O_2 (which is a triplet biradical in its ground state). Dioxygen does not suppress fluorescence (FL) of electronically excited singlet states but functions as an efficient quencher for triplet states. The removal of dioxygen from the solution may result in a substantially greater contribution of phosphorescence (PH); this was demonstrated, in particular, in the study of the CL that accompanies decomposition of tetramethyldioxetane (TMD).[342] We used a similar expedient and found that thermal (46 °C) decomposition of both non-deuterated and deuterated **1a** in acetone purified from traces of oxygen was actually accompanied by CL in the visible region;[13] the CL maximum occurs within a band with λ_{max} = 390 nm, typical of the phosphorescence of the resulting electronically excited triplet state of methyl acetate (MA*).[14]

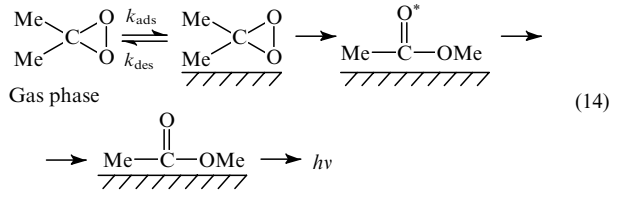


(13)

The decay of CL follows first-order kinetics (for non-deuterated **1a**, $k_{eff} = 8.5 \times 10^{-3}$ s^{-1}).[13] The quantum yield of CL ($\varphi_{CL} = 2.2 \times 10^{-11}$ and 6×10^{-11} Einstein mol^{-1} for non-deuterated and deuterated dioxirane, respectively) and the yield of excited MA [φ*(MA) = 10^{-4}%] are relatively low‡ compared, for example, with the φ* values for ketones formed upon decomposition of 1,2-dioxetanes[21,22] (the yield of excitation of triplet acetone in the decomposition of TMD is 37%). This low φ* value for MA* is evidently due to 'dark' decomposition of **1a** occurring in parallel (in the absence of O_2 at high temperatures) by a radical chain mechanism (see Section III). However, according to energy estimates, the reaction sequence presented in Scheme 7 cannot lead to excitation of MA.[13] Therefore, reaction (13) is the most probable CL channel. Apparently, this reaction proceeds in parallel with those shown in Scheme 7, but in the absence of O_2, its contribution must be low, which accounts for the low intensity of luminescence. Under 'normal' conditions, isomerisation also occurs, however CL is suppressed almost completely by the O_2 present in the system.

It should be noted that reaction (13), according to which the excited state is formed upon a direct isomerisation event without fragmentation of the molecule, is a very uncommon process.

Decomposition of dimethyldioxirane **1a** upon sorption from the gas phase on the Silipor surface is accompanied by much brighter CL than its decomposition in solution (MA* is the emitter).[11]



(14)

In fact, the minimum possible CL characteristics under these conditions were estimated[16,343] to be two orders of magnitude larger ($\varphi_{CL} \geqslant 4 \times 10^{-9}$ Einstein mol^{-1};φ*(MA) > 0.01 %)§ than the corresponding values for decomposition of **1a** in oxygen-free acetone solutions.[13] Among other reasons, this may be due to lower efficiency of quenching processes on the Silipor surface. However, in our opinion, the main reason for the increase in the CL yield on the Silipor surface lies in the mechanism of dioxirane decomposition; whereas in the solution in the absence of O_2 at elevated temperatures, the 'dark' radical chain decomposition (see Scheme 7) is the predominant process, on the Silipor surface, where radical reactions are much less efficient, chemiluminescent isomerisation [reaction (14)] becomes the major channel for the consumption of **1a**.

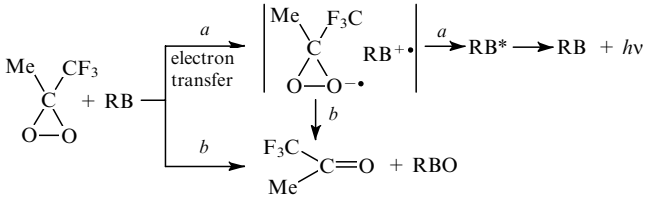
The kinetics of the decay of CL during decomposition of dimethyldioxirane **1a** adsorbed on a Silipor surface is described by a first-order equation; however, the effective rate constant (k_{eff} = 0.01 s^{-1}), found from the kinetic curves for CL decay plotted on the semilogaithmic coordinates, scarcely depends on the temperature (in the range 65–90 °C).[16,343] Evidently, the observed rate constant, which is an effective value, depends not only on the isomerisation constant of the dioxirane **1a** but also on the adsorption equilibrium (k_{des}/k_{ads}), so that the increase in the rate constant for the desorption of the dioxirane **1a** from the Silipor surface following an increase in the temperature makes up for the increase in the isomerisation rate constant, the k_{eff} value remaining almost invariable.

It is noteworthy that low-intensity chemiluminescence is also observed in a cell containing no Silipor.[11] This may be due to both isomerisation of the dioxirane **1a** in the gas phase and its decomposition on the internal surface of the cell. The addition of Silipor to a solution of the dioxirane **1a** in acetone causes a short burst of luminescence, characterised by a relatively low intensity.[343]

2. Activated chemiluminescence

Luminescence activation by polyaromatic hydrocarbons is widely used to study the CL arising during oxidation of hydrocarbons[344–348] or decomposition of 1,2-dioxetanes.[21,22,349–352] Taking the reaction of the dioxirane **1b** with rubrene (RB) as an example, Adam, Curci, *et al.*[6] demonstrated the applicability of the luminescence activation method to detection of CL during decomposition of dioxiranes.

Scheme 11



It was suggested that rubrene activates the CIEEL mechanism (Scheme 11, pathway *a*). In addition to CIEEL, there is also another channel of dioxirane consumption, namely, oxidation of rubrene (Scheme 11, pathway *b*), which decreases the CL intensity.[6] Detection of the EPR signal of the radical cation **41**$^{+\bullet}$, formed in the reaction of pyrene with the dioxirane **1b** by reaction (12), is an additional argument pointing to the CIEEL mechanism in the chemiluminescence reactions of dioxiranes.[272]

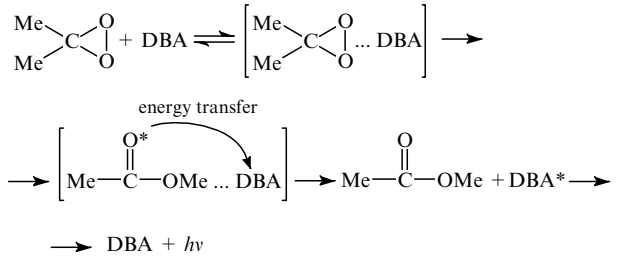
The reaction of the dioxirane **1a** with PAH is also accompanied by CL. Thus CL has been discovered in the thermolysis of the dioxirane **1a** (35 °C, Ar) in the presence of 9,10-diphenylanthracene (DPA), 9,10-dibromoanthracene (DBA) and anthracene (A).[10] In all cases, the activators acted as the emitters of the observed luminescence (the maximum CL intensity increases in

‡ Since no data on the yield of emission of MA (φ_{emis}) can be found in the literature, this value is assumed to be at least not greater (actually, it must be smaller) than the φ_{emis} values for related compounds, ketones, for which $\varphi_{emis} = 10^{-5}$. Thus, from here on, we should imply the minimum possible CL characteristics.

§ The CL characteristics were estimated under the assumption that all the dioxirane present in the cell with Silipor is accumulated on the sorbent surface; in reality, this proportion can be only several percent and, hence, the real CL yield and φ*(MA) are an order of magnitude greater.

the sequence $I_A < I_{DPA} < I_{DBA}$). The mechanism of activation of CL depends on the nature of the activator. Based on experimental results, it has been suggested [10, 343] that anthracene and 9,10-diphenylanthracene, which are oxidised during the reaction, activate the CIEEL mechanism, and 9,10-dibromoanthracene activates luminescence by the mechanism of energy transfer from MA* to the activator (Scheme 12).

Scheme 12



In the presence of DBA, the CL decay follows first-order kinetics; however, the observed rate constant depends on the activator concentration, which implies that 9,10-dibromoanthracene catalyses the dioxirane decomposition.[123, 343] However, anthracene and DPA influence the process kinetics in a more complicated way than DBA: the curve for the luminescence decay has two sections, 'fast' and 'slow' (Fig. 6).[123, 343] It can be suggested that decomposition of the dioxirane **1a** accounts for only the 'fast' section of the curve (section *1*), whereas an intermediate labile compound (perhaps, of the peroxide type), resulting from oxidation of the activators by the dioxirane, is responsible for the luminescence in the slow section (section *2*). Indeed, after the CL kinetics had reached section *2* (Fig. 6) and acetone had been completely evaporated from the reaction cell, the addition of a new portion of acetone restored the luminescence intensity nearly up to the previous level.[123, 343] Similar kinetics observed in the presence of anthracene may be due to analogous reasons.

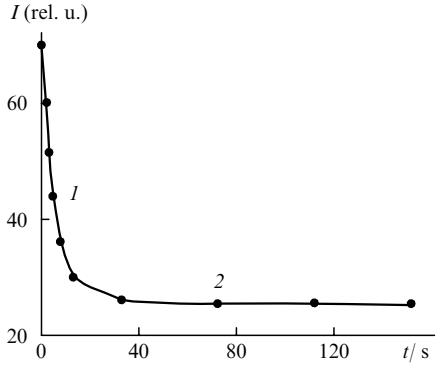


Figure 6. Kinetic curve for the decay of luminescence in the presence of DPA. $[DPA]_0 = 6.7 \times 10^{-4}$ mol litre^{-1}, $[\mathbf{1a}]_0 = 2 \times 10^{-2}$ mol litre^{-1}, acetone, 35 °C.

Besides PAH, luminescent metal compounds can also be used to activate the CL of dioxiranes. Thus the reaction of Ru(bipy)$_3$Cl$_2$ with dimethyldioxirane **1a** in solution is accompanied by bright CL,[15] emitted by Ru(II)* (Fig. 7).

The CL decay obeys a first-order equation, the observed first-order rate constant for the CL decay (k_{CL}) being proportional to the Ru(II) concentration: $k_{CL} = k_1 + k_2[Ru(II)]$. The activation parameters found from the temperature dependence of the bimolecular rate constant for the reaction k_2 are the following: $E_a = 9.6 \pm 1.6$ kcal mol^{-1}, $\log A = 9.1 \pm 1.0$. It can be seen that the reaction of Ru(II) with the dioxirane **1a** has a markedly lower (by $\sim$13–14 kcal mol^{-1}) activation energy than non-catalysed

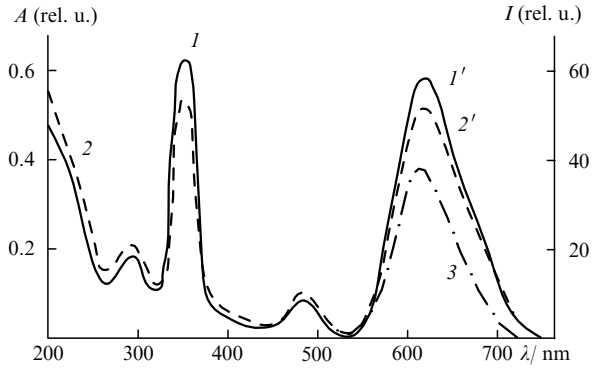
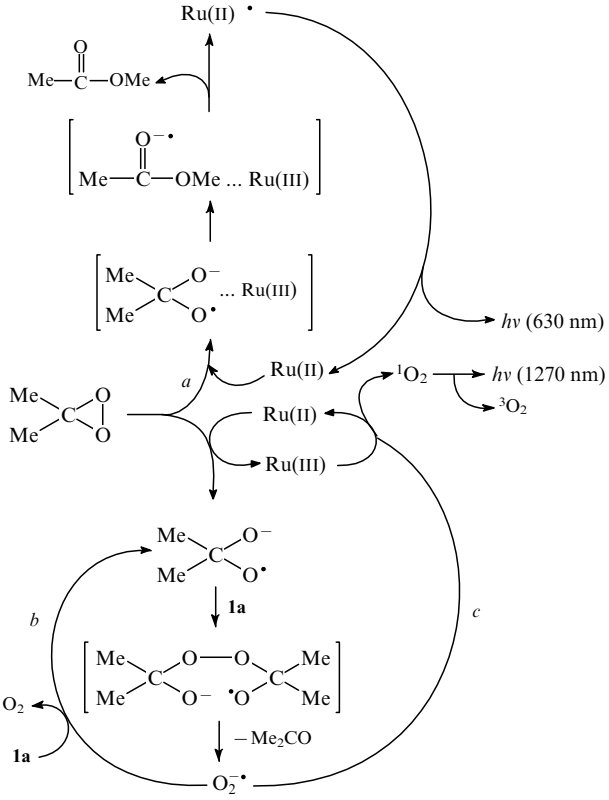


Figure 7. Absorption (*1*, *2*) and photoluminescence (*1′*, *2′*) spectra of Ru(II) ($[Ru(II)] = 5 \times 10^{-6}$ mol litre^{-1}, CH_3CN, 25 °C): (*1*, *1′*) before the reaction with the dioxirane **1a**; (*2*, *2′*) after the reaction with **1a** ($[\mathbf{1a}] = 2 \times 10^{-2}$ mol litre^{-1}); (*3*) chemiluminescence spectrum {$[Ru(II)] = 1.25 \times 10^{-4}$ mol litre^{-1}, $[\mathbf{1a}] = 6 \times 10^{-3}$ mol litre^{-1}}.

decomposition,[8, 118] because the ruthenium complex substantially catalyses the dioxirane decomposition. For $[Ru(II)] = 1.25 \times 10^{-4}$ mol litre^{-1}, the rate of catalysed decomposition of the dioxirane **1a** at 40 °C is greater than the rate of non-catalysed decomposition by a factor of 170 (!).[15]

Apparently, the activation of Ru(II)* luminescence and at least one pathway of the dioxirane decomposition catalysed by the ruthenium complex (Scheme 13) occur by the CIEEL mechanism, as has been shown for the reaction of Ru(II) with 1,2-dioxetanes.[353–357]

Scheme 13



Comparison of the photoluminescence and absorption spectra of Ru(II) before and after completion of the reaction (see Fig. 7) indicates that the reaction of the Ru(II) complex with dioxirane leads to oxidation of the complex; this, however, has no influence on the CL kinetics and does not distort the results because noticeable changes in the spectra can be observed only when a

4×10^3-fold excess of the dioxirane **1a** is present, whereas most of the kinetic measurements were carried out at lower ratios of **1a** to Ru(II).[15]

The CL quantum yield found from the plot for the light sum *versus* concentration (Fig. 8) using the equation $S = \varphi^*(\mathrm{Ru})\,\varphi_{\mathrm{FL}}\,k_2[\mathrm{Ru(II)}]_0[\mathbf{1a}]_0/(k_1 + k_2[\mathrm{Ru(II)}]_0)$ is equal to $\varphi_{\mathrm{CL}} = (9.5 \pm 3) \times 10^{-5}$ Einstein mol^{-1}, and the yield of excitation of Ru(II) (with allowance for the fact that the yield of ruth-enium emission $\varphi_{\mathrm{FL}} = 0.0095$) equals $\varphi^*(\mathrm{Ru}) = 0.01 \pm 0.005$.[15] The CL characteristics obtained indicate that the dioxirane **1a** – ruthenium complex system is a fairly bright chemiluminescence system. However, the φ^*(Ru) value for the reaction of Ru(II) with 1,2-dioxetanes is much greater (0.2).[357] Among other factors, the low ruthenium excitation yield in the CIEEL reaction of Ru(II) with the dioxirane **1a** may be due to the existence of a parallel channel for the dioxirane consumption, which yields no excited Ru(II). Below we demonstrate that this channel actually exists.

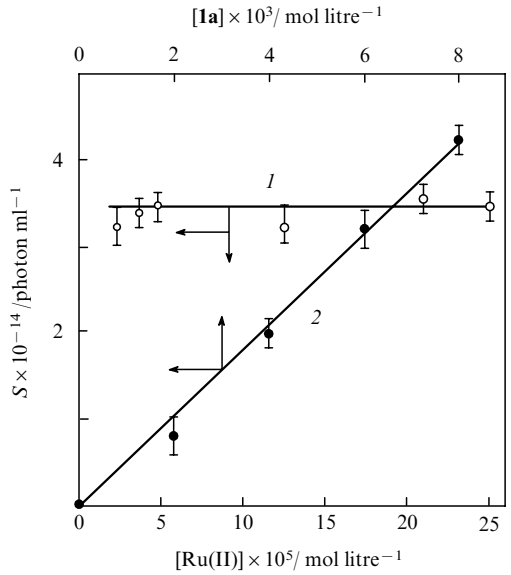


Figure 8. Chemiluminescence light sum in the reaction of the dioxirane **1a** with Ru(II) *vs* the concentration of Ru(II) (straight line *1*) ([**1a**] = 6×10^{-3} mol litre^{-1}) and the concentration of **1a** (straight line *2*) ([Ru(II)] = 1.25×10^{-4} mol litre^{-1}).

The catalytic activity of Ru(II) increases appreciably on excitation of the complex,[15] which is in good agreement with the theory of electron transfer. In fact, the k_2 value is known to depend on the oxidation potential of the activator (E_{Ox}) and the reduction potential of the peroxide (E_{Red}) according to the following equation:

$$k_2 = A \exp\left[-\frac{E_{\mathrm{Ox}} - E_{\mathrm{Red}} - e^2/\varepsilon R_0}{RT}\right], \qquad (15)$$

where e is the electron charge, ε is the dielectric constant of the solvent and R_0 is the distance between ions in the transition state. Since the oxidation potential of Ru(II)* decreases by the energy of excitation,[358] *i.e.*, $E^*_{\mathrm{Ru(II)^*/Ru(III)}} = E_{\mathrm{Ru(II)/Ru(III)}} - E^* = 1.29 - 2.12 = -0.83$ V, then, in conformity with Eqn (15), an increase in k_2 by several orders of magnitude should be expected. In fact, the Stern quenching constant (K), found from the linear section of the kinetics of quenching of Ru(II)* by dioxirane using the Stern–Volmer equation

$$\frac{\varphi_0}{\varphi} = \frac{\tau_0}{\tau} = 1 + K[\mathrm{Q}], \qquad (16)$$

(φ_0 and τ_0 are the quantum yield and the decay time of the luminescence without quencher Q, and [Q] is the quencher concentration), is the following: $K = k_{\mathrm{Q}}\,\tau_0 = 1800 \pm 200$ litre mol^{-1} [k_{Q} is the rate constant for the interaction of Ru(II)* with **1a**]. From this it follows that the catalytic activity of Ru(II) increases on excitation by a factor of more than 8×10^7.[15] It can be seen from Fig. 9 that at [**1a**] > 2.5×10^{-4} mol litre^{-1}, a negative deviation from the linear Stern–Volmer dependence is observed, obviously, due to the apparent decrease in the quenching efficiency caused by the recovery of the excited Ru(II) complex.

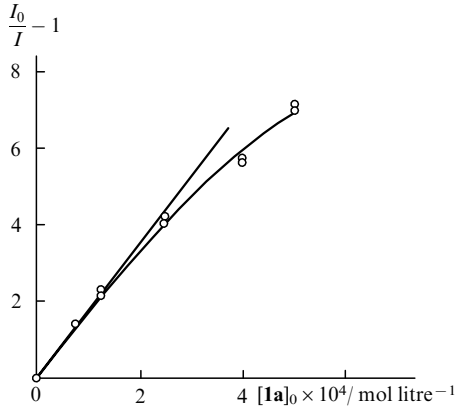
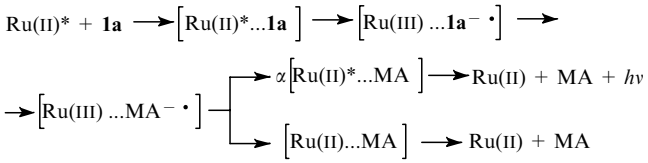


Figure 9. Kinetics of quenching of Ru(II) photoluminescence by the dioxirane **1a** in the coordinates of the Stern–Volmer equation. $\lambda_{\mathrm{excit}} = 450$ nm, [Ru(II)] = 2.5×10^{-5} mol litre^{-1}, 16 °C.



α is the excitation regeneration coefficient.

The calculation of the excitation regeneration coefficient gives the value $\alpha = 0.30 \pm 0.01$, which is much greater than φ^*[Ru(II)] for the reaction of **1a** with non-excited ruthenium. This leads to the conclusion that the contribution of the catalysed isomerisation of **1a** occurring by the reversible electron transfer mechanism (see Scheme 13, pathway *a*) increases markedly.[15]

As noted above, the relatively low φ^*[Ru(II)] value for the reaction of Ru(II) with the dioxirane **1a** (compared to this value for the reaction with 1,2-dioxetanes) may be due to the occurrence of a parallel channel of consumption of **1a**, which does not give excited Ru(II). This route actually does exist but this is not a dark reaction! On the contrary, it is accompanied by very bright CL, which occurs in the infrared region (1270 nm), indicating the formation of singlet oxygen in the system.[17, 343] The yield of $^1O_2$ based on the decomposed dioxirane **1a** in the Me_2CO–CD_3CN (1 : 2) system is 0.03%. It is notable that the kinetics of the IR CL decay, unlike that for the Ru(II)* luminescence in the visible region of the spectrum, follows a fairly complex pattern (Fig. 10).[17, 343] Thus, the Ru(II)–**1a** system contains two luminescence emitters,[15, 17, 343] Ru(II)* in the visible region and $^1O_2$ in the infrared region. A possible pathway to $^1O_2$ is the reaction of Ru(II) with the dioxirane **1a** by the electron chain mechanism (Scheme 13, pathways *b* and *c*). Pathway *b* is similar to that found in the I^-–**1b** system (the Adam–Curci system[321]) (see Scheme 10) with the only difference that in this case, Ru(II) serves as the electron donor. However, unlike the I^-–**1b** system,[321] in the Ru(II)–**1a** system, the oxidised trivalent ruthenium can be reduced to recover the initial divalent species (Scheme 13, pathway *c*), which apparently gives rise to the singlet oxygen [the interaction of Ru(III) with the superoxide ion is known to lead to the generation of $^1O_2$].[359]

Thus, in the reaction of Ru(III) with **1a**, the dioxirane is consumed, in all probability, *via* two competing pathways,

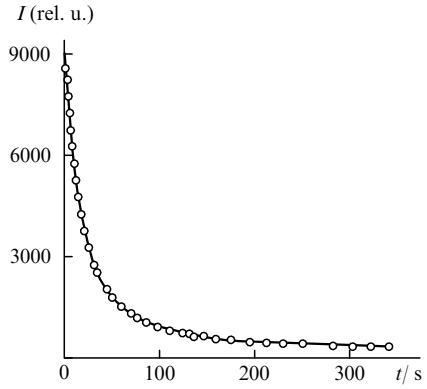


Figure 10. Typical kinetic curve for the decay of the $^1O_2$ chemiluminescence (IR region) in the reaction between Ru(II) and the dioxirane **1a** (25 °C, Ar, $[\mathbf{1a}]_0 = 5.25 \times 10^{-2}$ mol litre^{-1}, $[Ru(II)]_0 = 1 \times 10^{-4}$ mol litre^{-1}, solvent $Me_2CO - CD_3CN$ (1 : 2)].

namely, the CIEEL mechanism to give excited Ru(II) (Scheme 13, pathway *a*) and the electron chain decomposition to give singlet oxygen (Scheme 13, pathways *b* and *c*). The reactions of other transition metals with dioxiranes might also give rise to singlet oxygen.¶

The above-described thermal decomposition of **1a** upon adsorption of the Silipor surface from the gas phase can be substantially enhanced by applying CL activators [DBA, DPA, Ru(II)] on the Silipor surface.[16, 343] For example, in the presence of Ru(II) or DPA (concentration of the additive 1×10^{-6} mol g^{-1}), the maximum luminescence intensity increases 100- and 10-fold, respectively. The activators function as the luminescence emitters, which are apparently activated in the same way as in solutions.[16, 343] The CL yield (0.03×10^{-5} Einstein mol^{-1})[165, 343] for the decomposition of **1a** in the presence of Ru(II) applied to the Silipor surface proved to be about three orders of magnitude lower than the CL yield observed in the reaction of **1a** with Ru(II) in solution.[15] Since the electron transfer is controlled by diffusion, this difference can be explained by the decrease in the rate of the diffusion of the reactants on passing from the homogeneous system (solution) to heterogeneous conditions (Silipor – gas phase).

It is of interest that in the **1a** – Ru(II) – Silipor system, no CL from singlet oxygen is observed.[16] Apparently, the diffusion restrictions prevent development of the processes shown by pathway *b* (or *c*) (see Scheme 13).

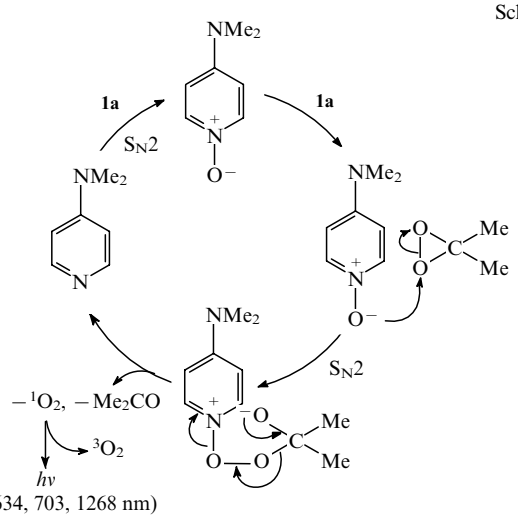
3. Other chemiluminescence reactions involving dioxiranes and dioxirane intermediates

Although the examples of formation of singlet oxygen in decomposition of dioxiranes are still few in number, they deserve attention, because the reactions described below are apparently far from being the last examples in which an extremely efficient oxidant (dioxirane) gives rise to another one, namely, $^1O_2$, which plays a very significant role in both chemistry and biology.[360 – 362]

Even the synthesis of dioxiranes itself is accompanied by the formation of $^1O_2$.[363] Non-catalysed decomposition of Caro's acid is known to give $^1O_2$.[364] Decomposition of Caro's acid catalysed by ketones is also accompanied by the evolution of oxygen (see Scheme 2). Previously,[4] this has been suggested to be singlet oxygen; later, this suggestion was confirmed experimentally by Lange and Brauer,[363] who observed CL of singlet oxygen at $\lambda = 1270$ nm during decomposition of Caro's acid induced by various ketones (acetone, butan-2-one, fluoroacetone, cyclohexanone, *etc.*). In addition to the detailed study of the reaction kinetics, they measured the yield of $^1O_2$ (in the case of acetone) per HSO_5^- molecule, which proved to be 0.5; this means that all the oxygen evolved is in the singlet state.[363]

Adam *et al.*[286] were the first to detect the evolution of $^1O_2$ in the reactions of isolated dioxirane. Previously, Murray[3] had noted that some *N*-oxides induce decomposition of **1a** with evolution of oxygen, which may be in the singlet state. Somewhat later, the Messeguer's group[263] found a catalytic effect of *N*-oxides on the decomposition of dioxiranes. Adam *et al.*[286] observed the same phenomenon in the oxidation of 4-dimethylaminopyridine by the dioxirane **1a**: 4-dimethylaminopyridine *N*-oxide formed in the reaction induced rapid decomposition of **1a** (Scheme 14). The reaction was accompanied by evolution of $^1O_2$ (at 37 °C, the fraction of $^1O_2$ in the total number of O_2 molecules was 5%), which was proved by CL registered in the infrared and visible regions of the spectrum. Luminescence in the visible region might be due to the dimol emission of $^1O_2$ (634 and 703 nm).[286]

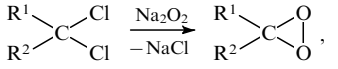
Scheme 14



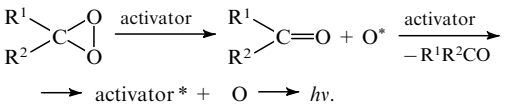
Finally, the third example of evolution of $^1O_2$ in the reactions of dioxiranes, namely, in the decomposition of **1a** catalysed by the complex $Ru(bipy)_3Cl_2$[17] was considered in detail above.

When drawing indirect analogy with 1,2-dioxetanes, it is noteworthy that only one example of the formation of $^1O_2$ during decomposition of 1,2-dioxetane (namely, 3-hydroxymethyl-3,4,4-trimethyl-1,2-dioxetane) has been reported.[365] The excitation of O_2 occurs *via* a trivial mechanism consisting in the transfer of energy from the triplet-excited carbonyl fragment (the product of dioxetane decomposition) to oxygen.

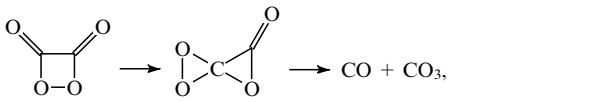
By now we have considered CL of isolated dioxiranes. However, several studies in which dioxiranes are considered as possible intermediates in various chemical and biochemical chemiluminescence systems have also been reported.[12, 97 – 101] In the 1980s, Steinfatt[97 – 100] published a series of studies, dealing with the reactions of a number of organic *gem*-dichlorides with sodium peroxide and hydroperoxide in the presence of aromatic sensitisers. These reactions were accompanied by fairly bright chemiluminescence. The yield of activated CL in the reaction of Na_2O_2 with 3,3-dichlorophthalide[97] was 10^{-3} Einstein mol^{-1} (!). Steinfatt also studied activated CL reactions of 1,8-$C_{10}H_6(COCl)_2$ with Na_2O_2[100] and Cl_2CO with NaOOH.[98] The following scheme was proposed to interpret the CL observed:

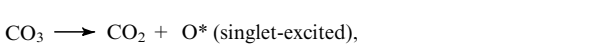


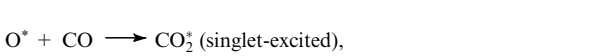
¶This should depend appreciably on the energy characteristics of the reaction. Thus we were unable to detect CL of singlet oxygen in the reaction of the dioxirane **1a** with Ce(III),[17, 343] apparently, due to the too high redox potential of the Ce(III)/Ce(IV) pair (1.4 V),[358] which precludes the transfer of an electron from Ce(III) to the dioxirane.

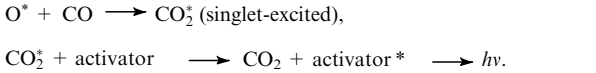


Dioxirane was also proposed as an intermediate to explain the CL of peroxyoxalate.[99]

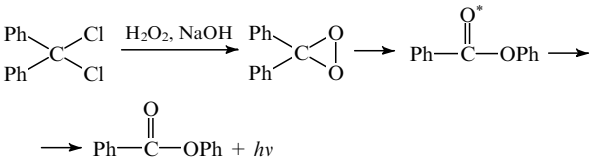








Later[12] we have observed non-sensitised CL in the $Ph_2CCl_2-H_2O_2-NaOH$ system, similar to the Steinfatt systems. The maximum of the luminescence intensity was concentrated in the range 400–450 nm, pointing to the possible formation of triplet phenyl benzoate, the product of isomerisation of diphenyldioxirane.[12]



It is significant that CL of diphenyldioxirane (provided that it is actually formed in this system) can be observed even in the absence of luminescence activators. On addition of Ru(II), the luminescence intensity increases by several orders of magnitude, the maximum intensity being directly proportional to the concentration of the complex. Apparently, in this case, as in the case of isomerisation of dimethyldioxirane **1a**, the CIEEL mechanism is involved.[12]

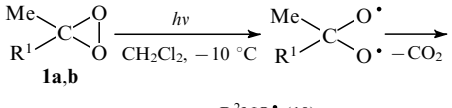
The formation of a dioxirane intermediate has also been assumed to interpret the mechanism of bioluminescence of bacteria.[101] The mechanism of excitation in these reactions cannot yet be considered to be conclusively established. The overall process is known to be catalysed by an enzyme — luciferase (E) — and consists in the oxidation of the reduced form of flavine mononuceotide ($FMNH_2$) by oxygen with participation of a long-chain aldehyde. A mechanism for the generation of luminescence was proposed[101] (Scheme 15); according to this mechanism, the reaction of O_2 with the complex $E \cdot FMNH_2$ yields C(4*a*)-peroxydihydroflavine **66**, which subsequently reacts with the aldehyde to give a tetrahedral intermediate **67**. These stages are in good agreement with known mechanisms. Presumably,[101] the next step includes the formation of a dioxirane intermediate and C(4*a*)-hydroxyflavine **68**. After that, there are two pathways for the generation of CL[101]

— decomposition of dioxirane to give an excited carboxylic acid and subsequent energy transfer on the hydroxyflavine **68**, which acts as the CL emitter; in this case, luminescence is activated by the energy transfer mechanism (Scheme 15, pathway *a*);

— the CIEEL mechanism in which the hydroxyflavine **68** acts as the fluorophore and the electron donor (Scheme 15, pathway *b*).

4. Photochemistry of dioxiranes

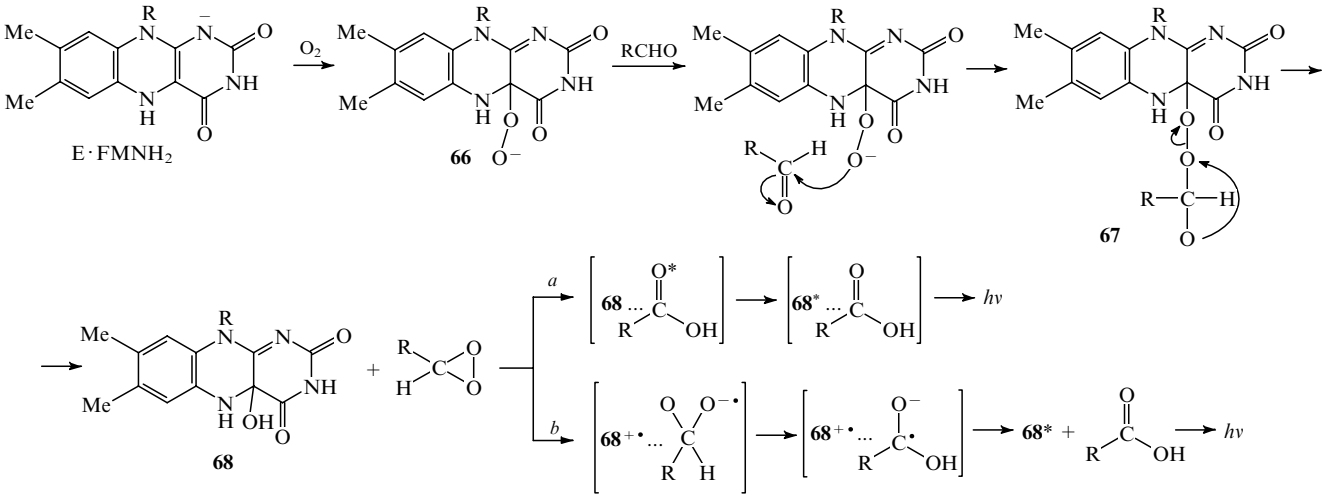
As many other peroxides, dioxiranes are sensitive to light; this was partially illustrated in Section III in relation to the dioxirane **1b** (see Schemes 3 and 4).[114] A similar type of behaviour is displayed by the dioxirane **1a**. Thus the quantum yield of photodecomposition of the dioxirane **1a** at 23 °C proved to be much greater than unity ($\varphi = 13.9 \pm 0.6$, 12.9 ± 1.7 and 13.1 ± 0.7 Einstein mol^{-1} at 340, 350 and 360 nm, respectively),[14] indicating that decomposition occurs by a radical chain mechanism. More evidence in favour of this mechanism is provided by the detection of adducts formed from alkyl radicals during the photolysis ($\lambda = 300$ nm) of the dioxiranes **1a** and **1b** in the presence of the trap **10** (**1b** completely decomposes under these conditions over a period of 30 min).[120]



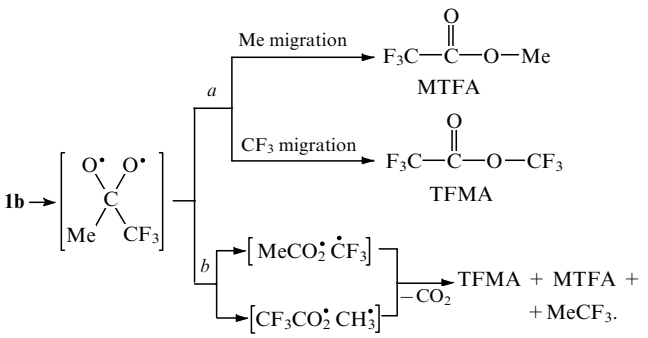
R^1 = Me (**1a**), CF_3 (**1b**).

However, at 77 K in a matrix, radical chain processes are less significant, and decomposition of **1b** ($\lambda > 300$ nm) yields 1,1,1-trifluoroethane (41%) and MTFA (51%) as the major reaction products together with small amounts of trifluoromethyl acetate (TFMA, 8%). Thus, the photolysis of the dioxirane **1b** in a matrix occurs as either isomerisation (Scheme 16, pathway *a*) or β-cleavage followed by cage recombination of the resulting radical pair (Scheme 16, pathway *b*) or follows simultaneously both channels.[114]

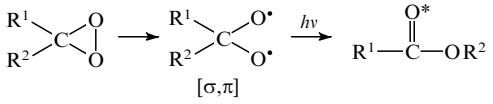
Scheme 15



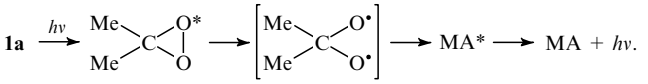
Scheme 16



It should be noted that isomerisation to give the corresponding ester is the main route in the low-temperature photolysis of a whole series of other dioxiranes obtained in a matrix.[33, 62, 65, 67, 69, 71, 72, 75, 80, 81] It has been suggested[7] that the $[\sigma,\pi]$-configuration of the dioxirane biradical should be responsible for the generation of an excited product.



Indeed, when the dioxirane **1a** in a matrix (77 K) is irradiated at a wavelength corresponding to its absorption band, phosphorescence of MA is observed (Fig. 11),[14] which is evidently due to the following process:



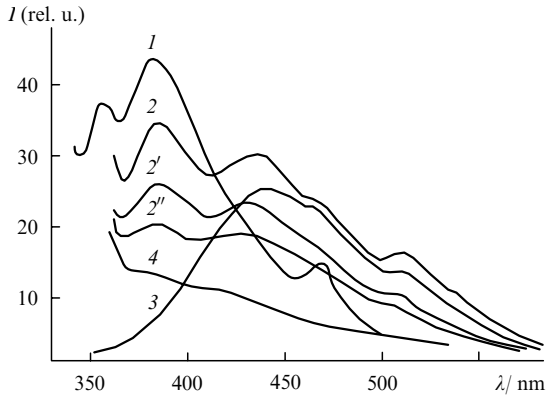
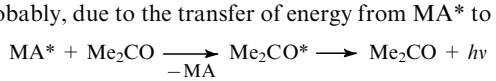


Figure 11. Phosphorescence spectra (77 K) of methyl acetate (*1*), dioxirane **1** (*2*, *2′*, *2″*) and acetone (*3*, *4*).
(*1*) λ_{excit} = 260 nm, $[MA]_0$ = 0.09 mol litre^{-1}, MeCN;
(*2*, *2′*, *2″*) λ_{excit} = 350 nm, $[\mathbf{1a}]_0$ = 0.09 mol litre^{-1}, acetone (spectra *2′* and *2″* were recorded at 25 min intervals under permanent irradiation);
(*3*) λ_{excit} = 320 nm; (*4*) λ_{excit} = 350 nm.

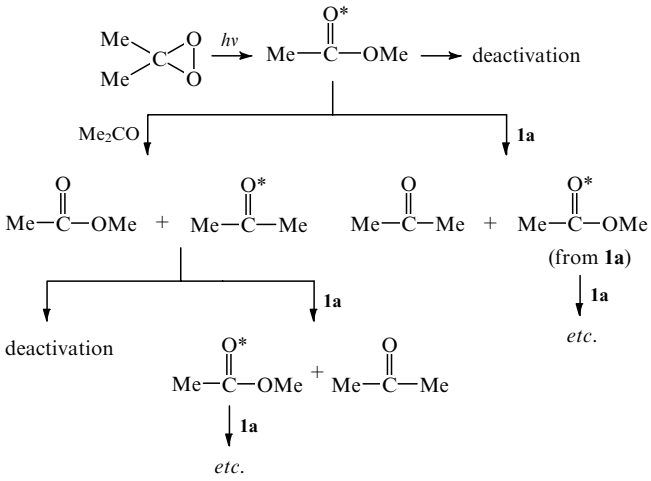
In addition to the triplet-excited MA*, photodecomposition of the dioxirane **1a** in a matrix affords triplet-excited acetone, probably, due to the transfer of energy from MA* to acetone.



The formation of MA* and the fact of energy migration suggest the existence of one more channel of dioxirane consumption by a quantum chain (QC) mechanism. In the 1960s, Shilov and Vedeneev[366] discovered experimentally a new class of chain gas-phase reactions involving vibrationally excited states. Somewhat later, in the 1970s, taking decomposition of 1,2-dioxetanes in solution as an example, the occurrence of chain processes with participation of species existing already in electronically excited states was demonstrated.[349, 367–369] In this case, a product of dioxetane decomposition — a triplet excited ketone — or an activator molecule is included in the chain propagation reactions.

Since decomposition of dioxiranes also gives a triplet-excited product (for example, decomposition of **1a** affords MA*), it can be expected that in the case of dioxiranes, QC processes are, in principle, quite probable (Scheme 17).

Scheme 17



Certainly, a solution of the dioxirane **1a** in acetone is far from being a perfect system for QC processes, first of all, due to the low efficiency of MA excitation and emission. In addition, the QC decomposition should be strongly hampered by the competing radical chain mechanism. However, other dioxiranes, in particular, those with chromophore-containing substituents, which give esters characterised by markedly larger emission yields, may prove to be prone to undergo photo and, perhaps, also thermal decomposition by the QC mechanism. Dimesityldioxirane **1j** seems quite promising in this respect.

VI. Conclusion

Dioxiranes remarkably combine two significant properties — the ability to act as strong oxidants and the ability to form products in the electronically excited states. It is these specific features that distinguish dioxiranes from other related compounds, in particular, 1,2-dioxetanes, the principal property of which is CL, or from a number of peroxy compounds, which have found application as oxidants in organic synthesis.

The high oxidative capacity of dioxiranes combined with the selectivity and mild conditions of reactions permitted researchers to perform a great number of oxidative transformations, which would have been impossible with other reagents. In addition, due to the availability of initial compounds and the ease of preparation of dioxiranes, these reagents can be used almost in any chemical laboratory.

Study of the CL of dioxiranes resulted in the discovery of a unique pathway to excited states. In fact, the rearrangement of dioxiranes into the corresponding esters initiated either thermally or photochemically is an exceptionally uncommon example of generation of an excited state directly upon an isomerisation event without fragmentation of the molecule (decomposition of 1,2-dioxetanes occurs *via* fragmentation of the molecule to give several products, one being in the excited state). A similar reaction route has been observed previously only for isomerisation of Dewar's benzene to excited Kekule's benzene.[370]

It can be conjectured that in the future, the chemistry of dioxiranes will develop along these lines. Without doubt, studies on the oxidative properties of dioxiranes and physicochemical

regularities of these reactions will be continued. Until now, the mechanism of decomposition of dioxiranes in the absence of oxidisable compounds has not been ultimately determined. The role of isomerisation in the set of other channels of dioxirane decomposition, which depend substantially not only on the external conditions but also on the structure of dioxiranes themselves, is still to be elucidated.

Despite the obvious difficulties, the search for the routes and conditions for the synthesis of new dioxiranes of various structures still remains a topical task. It is beyond doubt that success along this line (the first successful steps are being taken [59, 80–83, 117]) would substantially extend the possibilities of studying the properties of this new class of peroxides. This refers both to oxidative transformations (in particular, with the outlook for the preparation of chiral dioxiranes suitable for attaining prochiral oxidation) and chemiluminescence. Thus decomposition of a dioxirane with chromophore-containing substituents, for example dimesityldioxirane **1j** already synthesised,[80, 81] can be accompanied by CL comparable with the CL of dioxetanes. The presence of these dioxiranes including some bisdioxiranes would be useful for the study of energy migration paths in a matrix, in solution or on a sorbent surface and also for the study of quantum chain and energy coupled reactions.[21, 371] However, we are sure that the study of CL of the dioxiranes **1a** and **1b** would provide not less impressive results. Apart from the CL of dioxiranes themselves, one should also expect luminescence during their oxidative reactions with various organic and organometallic substrates, oxidation of which by other oxidants (XeF_2, XeO_3, O_2, *etc.*) results in bright CL.[372–374] This is equally true for inorganic compounds. It is known that in the recent decades, a large number of bright CL reactions accompanying oxidation of low-valence uranium species (*e.g.*, by xenon compounds, XeF_2 or XeO_3) were discovered.[375–386] If dioxiranes are included in the set of oxidants, high excitation yields can be expected in these systems.

A lot of interesting discoveries would result from combination of the chemistry of dioxiranes and 1,2-dioxetanes with the chemistry of complexes of *f*- and *d*-elements.[387–401] A dioxirane–lanthanide complex system may prove to be the second system, after a similar dioxetane-containing system, in which a new class of chain processes — quantum-chain reactions with energy branching — can be observed.[399–401]

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References

1. R W Murray, R Jeyaraman *J. Org. Chem.* **50** 2847 (1985)
2. R W Murray *Mol. Struct. Energ.* **6** 311 (1988)
3. R W Murray *Chem. Rev.* **89** 1187 (1989)
4. W Adam, R Curci, J O Edwards *Acc. Chem. Res.* **22** 205 (1989)
5. R Curci, in *Advances in Oxygenated Processes* Vol. 2 (Ed. A L Baumstark) (Greenwich: JAI Press, 1990) p. 1
6. W Adam, L P Hadjiarapoglou, R Curci, R Mello, in *Organic Peroxides* Ch. 4 (Ed. W Ando) (New York: Wiley, 1992) p. 195
7. W Adam, L Hadjiarapoglou *Top. Curr. Chem.* **164** 45 (1993)
8. R Curci, A Dinoi, M F Rubino *Pure Appl. Chem.* **67** 811 (1995)
9. E L Clennan *Trends Org. Chem.* **5** 231 (1995)
10. D V Kazakov, N N Kabal'nova, A I Voloshin, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 2286 (1995) [a]
11. D V Kazakov, A I Voloshin, N N Kabal'nova, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 2582 (1996) [a]
12. A M Nazarov, A I Voloshin, G A Yamilova, V D Komissarov, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 2593 (1996) [a]
13. D V Kazakov, A I Voloshin, N N Kabal'nova, S L Khursan, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 477 (1997) [a]
14. D V Kazakov, A I Voloshin, N N Kabal'nova, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 938 (1997) [a]
15. D V Kazakov, A I Voloshin, N N Kabal'nova, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 1138 (1997) [a]
16. D V Kazakov, A I Voloshin, N N Kabal'nova, V V Shereshovets, V P Kazakov *Mendeleev Commun.* 49 (1998)
17. D V Kazakov, A I Voloshin, V V Shereshovets, V N Yakovlev, V P Kazakov *Mendeleev Commun.* 169 (1998)
18. W Adam, in *The Chemistry of Functional Groups: Peroxides.* (Ed. S Patai) (New York: Wiley, 1983) p. 829
19. G B Schuster, S P Schmidt *Adv. Phys. Org. Chem.* **18** 187 (1982)
20. R F Vasil'ev, in *Biokhemilyuminestsentsiya* (The Biochemiluminescnce) (Ed. A I Zhuravlev) (Moscow: Nauka, 1983) p. 31
21. G L Sharipov, V P Kazakov, G A Tolstikov *Khimiya i Khemilyuminestsentsiya 1,2-Dioksetanov* (The Chemistry and Chemiluminescnce of 1,2-Dioxetanes) (Moscow: Nauka, 1990)
22. C R Saha-Müller, W Adam, in *Comprehensive Heterocyclic Chemistry II* Vol. 1B (Ed. A Padwa) (Oxford: Pergamon Press, 1996) p. 1041
23. R Criegee, G Wenner *Liebigs Ann. Chem.* **564** 9 (1949)
24. T Sugawara, H Iwamura, H Hayashi, A Sekiguchi, W Ando, M T H Liu *Chem. Lett.* 1261 (1983)
25. T A Hinrichs, V Ramachandran, R W Murray *J. Am. Chem. Soc.* **101** 1282 (1979)
26. R W Murray, R Banavali *Tetrahedron Lett.* **24** 2327 (1983)
27. S Kumar, R W Murray *J. Am. Chem. Soc.* **106** 1040 (1984)
28. W Sander *Angew. Chem., Int. Ed. Engl.* **29** 344 (1990)
29. W Sander, A Kirschfeld, W Kappert, S Muthusamy, M Kiselewsky *J. Am. Chem. Soc.* **118** 6508 (1996)
30. R L Kuczkowski, in *Ozone and Carbonyl Oxides* Vol. 2 (Ed. A Padwa) (New York: Wiley, 1984) p. 197
31. J C Scaiano, W G McGimpsey, H L Casal *J. Org. Chem.* **54** 1612 (1989)
32. W Sander, G Bucher, S Wierlacher *Chem. Rev.* **93** 1583 (1993)
33. W Sander, A Kirschfeld, in *Advances in Strain in Organic Chemistry* Vol. 4 (London: JAI Press, 1995) p. 1
34. A Bravo, F Fontana, G Fronza, A Mele, F Minisci *J. Chem. Soc., Chem. Commun.* 1573 (1995)
35. F Minisci, L Zhao, F Fontana, A Bravo *Tetrahedron Lett.* **36** 1697 (1995)
36. D V Kazakov, N N Kabal'nova, S L Khursan, V V Shereshovets *Izv. Akad. Nauk, Ser. Khim.* 694 (1997) [a]
37. R Curci, A Dinoi, C Fusco, M A Lillo *Tetrahedron Lett.* **37** 249 (1996)
38. C Fusco, M Fiorentino, A Dinoi, R Curci, R A Krause, D Kuck *J. Org. Chem.* **61** 8681 (1996)
39. W Adam, R Curci, L D'Accolti, A Dinoi, C Fusco, F Gasparrini, R Kluge, R Paredes, M Schulz, A K Smerz, L Angela Veloza, S Weinkoetz, R Winde *Chem. Eur. J.* **3** 105 (1997)
40. R Jeyaraman, R W Murray *J. Am. Chem. Soc.* **106** 2462 (1984)
41. F J Lovas, R D Suenram *Chem. Phys. Lett.* **51** 453 (1977)
42. R D Suenram, F J Lovas *J. Am. Chem. Soc.* **100** 5117 (1978)
43. R I Martinez, R E Huie, J T Herron *Chem. Phys. Lett.* **51** 457 (1977)
44. S A Kafaki, R I Martinez, J T Herron *Mol. Struct. Energ.* **6** 283 (1988)
45. R W Murray, R Jeyaraman, in *Polynuclear Aromatic Hydrocarbons: Tenth International Symposium on a Decade of Progress* (Eds M W Cooke, A J Dennis) (Columbus, OH: Battelle Press, 1985) p. 595
46. R W Murray, M K Pillay, M J Snelson, in *Polynuclear Aromatic Hydrocarbons: Measurements, Means, and Metabolism* (Eds M Cooke, K Loening, J Merritt) (Columbus, OH: Battelle Press, 1991) p. 615
47. R W Murray, W Kong *Polycyclic Aromat. Compd.* **5** 139 (1994)
48. A V Baeyer, V Villiger *Berichte* **32** 3625 (1899)
49. C D Harries *Liebigs Ann. Chem.* **374** 288 (1910)
50. US P. 3 632 606; *Chem. Abstr.* **76** 99 638 (1972)
51. R E Keay, G A Hamilton *J. Am. Chem. Soc.* **97** 6876 (1975)
52. R E Keay, G A Hamilton *J. Am. Chem. Soc.* **98** 6578 (1976)
53. W A Pryor, C K Govindan, D F Church *J. Am. Chem. Soc.* **104** 7563 (1982)

54. T A Walter, J J Bufalini, B W Gay Jr *Environ. Sci. Technol.* **11** 382 (1977)
55. R H Eastman, R M Silverstein *J. Am. Chem. Soc.* **75** 1493 (1953)
56. H E Smith, R H Eastman *J. Am. Chem. Soc.* **83** 4274 (1961)
57. H E O'Neal, C Blumstein *Int. J. Chem. Kinet.* **5** 397 (1973)
58. S Vaccani, H Kuhne, A Bauder, H H Gunthard *Chem. Phys. Lett.* **50** 187 (1977)
59. K R Kopecky, Y Xie, J Molina *Canad. J. Chem.* **71** 272 (1993)
60. A Sekiguchi, W Ando *J. Chem. Soc., Chem. Commun.* 575 (1979)
61. P S Bailey *Ozonation in Organic Chemistry* Vol. 1 (New York: Academic Press, 1978)
62. O L Chapman, T C Hess *J. Am. Chem. Soc.* **106** 1842 (1984)
63. G A Bell, I R Dunkin *J. Chem. Soc., Chem. Commun.* 1213 (1983)
64. I R Dunkin, G A Bell *Tetrahedron* **41** 339 (1985)
65. I R Dunkin, C J Shields *J. Chem. Soc., Chem. Commun.* 154 (1986)
66. G A Bell, I R Dunkin, C J Shields *Spectrochim. Acta, Part A* **41** 1221 (1985)
67. G A Ganzer, R S Sheridan, M T H Liu *J. Am. Chem. Soc.* **108** 1517 (1986)
68. W Sander *Angew. Chem., Int. Ed. Engl.* **25** 255 (1986)
69. W Sander *J. Org. Chem.* **54** 333 (1989)
70. W Sander *Angew. Chem., Int. Ed. Engl.* **24** 988 (1985)
71. W Sander *J. Org. Chem.* **53** 121 (1988)
72. W Sander *J. Org. Chem.* **53** 2091 (1988)
73. S Murata, H Tomioka, T Kawase, M Oda *J. Org. Chem.* **55** 4502 (1990)
74. H Tomioka, K Komatsu, M Shimizu *J. Org. Chem.* **57** 6216 (1992)
75. G Bucher, W Sander *Chem. Ber.* **125** 1851 (1992)
76. W Sander *Spectrochim. Acta, Part A* **43** 637 (1987)
77. S Wierlacher, W Sander, M T H Liu *J. Org. Chem.* **57** 1051 (1992)
78. J R Sodeau, L J Whyte *J. Chem. Soc., Faraday Trans.* **87** 3725 (1991)
79. S Wierlacher, W Sander, C Marquardt, E Kraka, D Cremer *Chem. Phys. Lett.* **222** 319 (1994)
80. A Kirschfeld, S Muthusamy, W Sander *Angew. Chem., Int. Ed. Engl.* **33** 2212 (1994)
81. W Sander, K Schroeder, S Muthusamy, A Kirschfeld, W Kappert, R Boese, E Kraka, C Sosa, D Cremer *J. Am. Chem. Soc.* **119** 7265 (1997)
82. A Russo, D D DesMarteau *Angew. Chem., Int. Ed. Engl.* **32** 905 (1993)
83. H Burger, P Weinrath, G A Arguello, B Julicher, H Willner, D D DesMarteau, A Russo *J. Mol. Spectrosc.* **168** 607 (1994)
84. W Ando, H Miyazaki, S Kohmoto *Tetrahedron Lett.* 1317 (1979)
85. W Ando, Y Kabi, H Miyazaki *Photochem. Photobiol.* **31** 191 (1980)
86. A Sekiguchi, Y Kabe, W Ando *J. Org. Chem.* **47** 2900 (1982)
87. T Tezuka, M Iwaki *Tetrahedron Lett.* **24** 3109 (1983)
88. T Tezuka, M Iwaki *Heterocycles* **22** 725 (1984)
89. T Tezuka, M Iwaki *J. Chem. Soc., Perkin Trans. 1* 2507 (1984)
90. T Tezuka, M Iwaki, Y Haga *J. Chem. Soc., Chem. Commun.* 325 (1984)
91. W Ando, R Sato, H Sonobe, T Akasaka *Tetrahedron Lett.* **25** 853 (1984)
92. W Ando, S Kohmoto, K Nishizawa *J. Chem. Soc., Chem. Commun.* 894 (1978)
93. W Ando, S Kohmoto, H Miyazaki, K Nishizawa, H Tsumaki *Photochem. Photobiol.* **30** 81 (1979)
94. M Rahman, M L McKee, P B Shevlin, R Sztyrbicka *J. Am. Chem. Soc.* **110** 4002 (1988)
95. W Adam, A Rodriquez *J. Am. Chem. Soc.* **102** 404 (1980)
96. W Adam, A Rodriquez *Tetrahedron Lett.* **22** 3509 (1981)
97. M Steinfatt *J. Chem. Res. (S)* 111 (1984)
98. M Steinfatt *J. Chem. Res. (S)* 211 (1984)
99. M Steinfatt *Bull. Soc. Chim. Belg.* **94** 85 (1985)
100. M Steinfatt *J. Chem. Res. (S)* 140 (1985)
101. F M Raushel, T O Baldwin *Biochem. Biophys. Res. Commun.* **164** 1137 (1989)
102. R E Montgomery *J. Am. Chem. Soc.* **96** 7820 (1974)
103. J O Edwards, R H Pater, R Curci, F Di Furia *Photochem. Photobiol.* **30** 63 (1979)
104. R Curci, M Fiorentino, L Troisi, J O Edwards, R H Pater *J. Org. Chem.* **45** 4758 (1980)
105. A R Gallopo, J O Edwards *J. Org. Chem.* **46** 1684 (1981)
106. G Cicala, R Curci, M Fiorentino, O Laricchiuta *J. Org. Chem.* **47** 2670 (1982)
107. R Curci, M Fiorentino, M R Serio *J. Chem. Soc., Chem. Commun.* 155 (1984)
108. L Cassidei, M Fiorentino, R Mello, O Sciacovelli, R Curci *J. Org. Chem.* **52** 699 (1987)
109. W Adam, Y-Y Chan, D Cremer, J Gauss, D Scheutzow, M Schindler *J. Org. Chem.* **52** 2800 (1987)
110. W Adam, J Bialas, L Hadjiarapoglou *Chem. Ber.* **124** 2377 (1991)
111. R Mello, M Fiorentino, O Sciacovelli, R Curci *J. Org. Chem.* **53** 3890 (1988)
112. M Singh, R W Murray *J. Org. Chem.* **57** 4263 (1992)
113. H K Chenault, S J Danishefsky *J. Org. Chem.* **54** 4249 (1989)
114. W Adam, R Curci, M E Gonzalez-Nunez, R Mello *J. Am. Chem. Soc.* **113** 7654 (1991)
115. M Ferrer, M Gibert, F Sanchez-Baeza, A Messeguer *Tetrahedron Lett.* **37** 3585 (1996)
116. M Gibert, M Ferrer, F Sanchez-Baeza, A Messeguer *Tetrahedron* **53** 8643 (1997)
117. R W Murray, M Singh, R Jeyaraman *J. Am. Chem. Soc.* **114** 1346 (1992)
118. L A Hull, L Budhai *Tetrahedron Lett.* **34** 5039 (1993)
119. A L Baumstark, M Beeson, P C Vasquez *Tetrahedron Lett.* **30** 5567 (1989)
120. W Adam, S E Bottle, R Mello *J. Chem. Soc., Chem. Commun.* 771 (1991)
121. R Mello, M Fiorentino, C Fusco, R Curci *J. Am. Chem. Soc.* **111** 6749 (1989)
122. M Ferrer, F Sanchez-Baeza, J Casas, A Messeguer *Tetrahedron Lett.* **35** 2981 (1994)
123. D V Kazakov, Candidate Thesis in Chemical Sciences, Institute of Organic Chemistry, Ural Scientific Centre, Russian Academy of Sciences, Ufa, 1997
124. A Dinoi, R Curci, P Carloni, E Damiani, P Stipa, L Greci *Eur. J. Org. Chem.* 871 (1998)
125. N N Kabal'nova, D V Kazakov, N M Shishlov, V V Sheresho-vets *Izv. Akad. Nauk, Ser. Khim.* 1552 (1996) [a]
126. V E Zubarev *Metod Spinovykh Lovushek* (The Method of Spin Traps) (Moscow: Moscow State University, 1984)
127. E Niki, S Yokoi, J Tsuchiya, Y Kamiya *J. Am. Chem. Soc.* **105** 1498 (1983)
128. P Neta, R E Hull, A B Ross *J. Phys. Chem. Ref. Data* **19** 413 (1990)
129. B Plesnicar, F Kovač, M Schara *J. Am. Chem. Soc.* **110** 214 (1988)
130. W A Pryor, D G Prier, D F Church *J. Am. Chem. Soc.* **105** 2883 (1983)
131. V B Kogan, V M Fridman, V V Kafarov *Spravochnik po Rastvorimosti* (Handbook on Solubility) (Moscow: Izd. Akad. Nauk. SSSR, 1961) Vol. 1, Book 1
132. S A Grabovski, D V Kazakov, N N Kabal'nova, S L Khursan, V V Shereshovets *React. Kinet. Catal. Lett.* **62** 179 (1997)
133. N J Turro, P Lechtken *J. Am. Chem. Soc.* **95** 266 (1973)
134. T Wilson, M E Landis, A L Baumstark, P D Bartlett *J. Am. Chem. Soc.* **95** 4766 (1973)
135. W H Richardson, F C Montgomery, P Slusser, M B Yelvington *J. Am. Chem. Soc.* **97** 2819 (1975)
136. E Kraka, Z Konkoli, D Cremer, J Fowler, H F Schaefer *J. Am. Chem. Soc.* **118** 10595 (1996)
137. B A Arndtsen, R G Bergan, T A Mobley, T H Peterson *Acc. Chem. Res.* **28** 154 (1995)
138. A Tenaglia, E Terranova, B Waegell *Tetrahedron Lett.* **30** 5271 (1989)
139. H-J Schneider, W Müller *J. Org. Chem.* **50** 4609 (1985)
140. H Mimoun, L Saussine, E Daire, M Postel, J Fischer, R Weisse *J. Am. Chem. Soc.* **105** 3101 (1983)
141. P S Bailey *Ozonization in Organic Chemistry* Vol. 2 (New York: Academic Press, 1982)
142. B S Jaynes, C L Hill *J. Am. Chem. Soc.* **117** 4704 (1995)
143. B Meunier *Chem. Rev.* **92** 1411 (1992)
144. A Ya Sychev, V G Isak *Usp. Khim.* **64** 1183 (1995) [*Russ. Chem. Rev.* **64** 1105 (1995)]
145. R W Murray, R Jeyaraman, L Mohan *J. Am. Chem. Soc.* **108** 2470 (1986)
146. W Adam, G Asensio, R Curci, M E Gonzalez-Nunez, R Mello *J. Org. Chem.* **57** 953 (1992)

147. R W Murray, H Gu *J. Org. Chem.* **60** 5673 (1995)
148. D Kuck, A Schuster *Z. Naturforsch., B Chem. Sci.* **46** 1223 (1991)
149. G Asensio, R Mello, M E Gonzalez-Nunez, G Castellano, J Corral *Angew. Chem., Int. Ed. Engl.* **35** 217 (1996)
150. K Pramod, P E Eaton, R Gilardi, J L Flippen-Anderson *J. Org. Chem.* **55** 6105 (1990)
151. R Mello, L Cassidei, M Fiorentino, C Fusco, R Curci *Tetrahedron Lett.* **31** 3067 (1990)
152. D S Teager, R K Murray Jr *J. Org. Chem.* **58** 5548 (1993)
153. D Kuck, A Schuster, C Fusco, M Fiorentino, R Curci *J. Am. Chem. Soc.* **116** 2375 (1994)
154. P Bovicelli, A Gambacorta, P Lupattelli *Tetrahedron Lett.* **33** 7411 (1992)
155. J T Dixon, C W Holzapfel, F R van Heerden *Synth. Commun.* **23** 135 (1993)
156. P Bovicelli, P Lupattelli, E Mincione, T Prencipe, R Curci *J. Org. Chem.* **57** 2182 (1992)
157. C Cerrè, A F Hofmann, C D Schteingart, W Jia, D Maltby *Tetrahedron* **53** 435 (1997)
158. P Bovicelli, P Lupattelli, E Mincione, T Prencipe, R Curci *J. Org. Chem.* **57** 5052 (1992)
159. W Adam, F Prechtl *Chem. Ber.* **124** 2369 (1991)
160. W Adam, A K Smerz *Tetrahedron* **52** 5799 (1996)
161. W Adam, M Shimizu *Synthesis* 560 (1994)
162. R Mello, L Cassidei, M Fiorentino, C Fusco, W Hümmer, V Jäger, R Curci *J. Am. Chem. Soc.* **113** 2205 (1991)
163. F Kovač, A L Baumstark *Tetrahedron Lett.* **35** 8751 (1994)
164. J K Crandall, M Zucco, R S Kirsch, D M Coppert *Tetrahedron Lett.* **32** 5441 (1991)
165. A Altamura, C Fusco, L D'Accolti, R Mello, T Prencipe, R Curci *Tetrahedron Lett.* **32** 5445 (1991)
166. R Curci, L D'Accolti, A Detomaso, C Fusco, K Takeuchi, Y Ohga, P E Eaton, Y C Yip *Tetrahedron Lett.* **34** 4559 (1993)
167. L D'Accolti, A Detomaso, C Fusco, A Rosa, R Curci *J. Org. Chem.* **58** 3600 (1993)
168. P Bovicelli, A Sanetti, P Lupattelli *Tetrahedron* **52** 10 969 (1996)
169. R Curci, L D'Accolti, A Dinoi, C Fusco, A Rosa *Tetrahedron Lett.* **37** 115 (1996)
170. W Adam, F Prechtl, M J Richter, A K Smerz *Tetrahedron Lett.* **34** 8427 (1993)
171. R Ballini, F Papa, P Bovicelli *Tetrahedron Lett.* **37** 3507 (1996)
172. M Abou-Elzahab, W Adam, C R Saha-Möller *Liebigs Ann. Chem.* 445 (1991)
173. G Asensio, G Castellano, R Mello, M E Gonzalez-Nunez *J. Org. Chem.* **61** 5564 (1996)
174. R Curci, L D'Accolti, M Fiorentino, C Fusco, W Adam, M E Gonzalez-Nunez, R Mello *Tetrahedron Lett.* **33** 4225 (1992)
175. P Bovicelli, A Sanetti, R Bernini, P Lupattelli *Tetrahedron* **53** 9755 (1997)
176. E V Dehmlow, N Heiligenstaedt *Tetrahedron Lett.* **37** 5363 (1996)
177. P E Sonnet, M E Lankin, G P McNeill *J. Am. Oil Chem. Soc.* **72** 199 (1995)
178. R Saladino, C Crestini, R Bernini, E Mincione, R Ciafrino *Tetrahedron Lett.* **36** 2665 (1995)
179. T M Hellman, G A Hamilton *J. Am. Chem. Soc.* **96** 1530 (1974)
180. R W Murray, D Gu *J. Chem. Soc., Perkin Trans. 2* 451 (1994)
181. J T Groves, T E Nemo, R S Myers *J. Am. Chem. Soc.* **101** 1032 (1979)
182. J T Groves, T E Nemo *J. Am. Chem. Soc.* **105** 6243 (1983)
183. R D Bach, J L Andres, M-D Su, J J W McDougall *J. Am. Chem. Soc.* **115** 5768 (1993)
184. F Minisci, L Zhao, F Fontana, A Bravo *Tetrahedron Lett.* **36** 1895 (1995)
185. A Bravo, F Fontana, G Fronza, F Minisci, A Serri *Tetrahedron Lett.* **36** 6945 (1995)
186. A Bravo, H-R Bjorsvik, F Fontana, F Minisci, A Serri *J. Org. Chem.* **61** 9409 (1996)
187. D V Kazakov, N N Kabal'nova, A I Voloshin, V V Shereshovets, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 1395 (1995) [a]
188. D V Kazakov, N N Kabalnova, S L Khursan, S A Grabovsky, V V Shereshovets *React. Kinet. Catal. Lett.* **60** 131 (1997)
189. D V Kazakov, D R Khusnullina, N N Kabal'nova, S L Khursan, V V Shereshovets *Izv. Akad. Nauk, Ser. Khim.* 1785 (1997) [a]
190. D R Khusnullina, D V Kazakov, N N Kabal'nova, S L Khursan, V V Shereshovets *Kinet. Katal.* **39** 8 (1998) [b]
191. V A Belyakov, R F Vasil'ev, G F Fedorova *Dokl. Akad. Nauk SSSR* **239** 344 (1978) [c]
192. G Asensio, R Mello, M E Gonzalez-Nunez, C Boix, J Royo *Tetrahedron Lett.* **38** 2373 (1997)
193. A Hofland, H Steinberg, T J de Boer *Recl. Trav. Chim. Pays-Bas* **104** 350 (1985)
194. W Adam, L Hadjiarapoglou, X Wang *Tetrahedron Lett.* **32** 1295 (1991)
195. A L Baumstark, P C Vasquez *J. Org. Chem.* **53** 3437 (1988)
196. A L Baumstark, C J McCloskey *Tetrahedron Lett.* **28** 3311 (1987)
197. W Adam, J Halasz, Z Jambor, A Levai, C Nemes, T Patonay, G Toth *J. Chem. Soc., Perkin Trans. 1* 395 (1996)
198. R W Murray, D L Shiang *J. Chem. Soc., Perkin Trans. 2* 349 (1990)
199. W Adam, L Hadjiarapoglou *Chem. Ber.* **123** 2077 (1990)
200. M Kurihara, S Ito, N Tsutsumi, N Miyata *Tetrahedron Lett.* **35** 1577 (1994)
201. C W Jones, J P Sankey, W R Sanderson, M C Rocca, S L Wilson *J. Chem. Res. (S)* 114 (1994)
202. D Yang, M-K Wong, Y-C Yip *J. Org. Chem.* **60** 3887 (1995)
203. R Curci, L D'Accolti, M Fiorentino, A Rosa *Tetrahedron Lett.* **36** 5831 (1995)
204. D Yang, X-C Wang, M-K Wong, Y-C Yip, M-W Tang *J. Am. Chem. Soc.* **118** 11 311 (1996)
205. D S Brown, B A Marples, P Smith, L Walton *Tetrahedron* **51** 3587 (1995)
206. M Schulz, S Liebsch, R Kluge, W Adam *J. Org. Chem.* **62** 188 (1997)
207. A Armstrong, P A Clarke, A Wood *J. Chem. Soc., Chem. Commun.* 849 (1996)
208. R W Murray, M Singh *Org. Synth.* **74** 91 (1997)
209. R M Coates, Z Ho, L Zhu *J. Org. Chem.* **61** 1184 (1996)
210. R W Murray, M Singh, N P Rath *J. Org. Chem.* **61** 7660 (1996)
211. G Person, M Keller, H Prinzbach *Liebigs Ann. Chem.* 507 (1996)
212. J K Crandall, D J Batal *J. Org. Chem.* **53** 1340 (1988)
213. J K Crandall, D J Batal *Tetrahedron Lett.* **29** 4791 (1988)
214. J K Crandall, D J Batal, D P Sebesta, F Lin *J. Org. Chem.* **56** 1153 (1991)
215. J K Crandall, E Rambo *J. Org. Chem.* **55** 5929 (1990)
216. J K Crandall, D J Batal, F Lin, T Reix, G S Nadol, R A Ng *Tetrahedron* **48** 1427 (1992)
217. W Adam, A Lgvai, J-Y Mgrour, C Nemes, T Patonay *Synthesis* 268 (1997)
218. W Adam, L P Hadjiarapoglou, A Meffert *Tetrahedron Lett.* **32** 6697 (1991)
219. W Adam, F Prechtl, M J Richter, A K Smerz *Tetrahedron Lett.* **36** 4991 (1995)
220. W Adam, L Hadjiarapoglou, B Nestler *Tetrahedron Lett.* **31** 331 (1990)
221. W Adam, L Hadjiarapoglou, A Smerz *Chem. Ber.* **124** 227 (1991)
222. C Baylon, I Hanna *Tetrahedron Lett.* **36** 6475 (1995)
223. G M Rubottom, M A Vasquez, D R Pelegrina *Tetrahedron Lett.* **15** 4319 (1974)
224. W Adam, L Hadjiarapoglou, V Jäger, J Klicić, B Seidel, X Wang *Chem. Ber.* **124** 2361 (1991)
225. L Troisi, L Cassidei, L Lopez, R Mello, R Curci *Tetrahedron Lett.* **30** 257 (1989)
226. W Adam, L Hadjiarapoglou, J Klicić *Tetrahedron Lett.* **31** 6517 (1990)
227. W Adam, L Hadjiarapoglou, V Jaeger, B Seidel *Tetrahedron Lett.* **30** 4223 (1989)
228. W Adam, R M Schuhmann *J. Organomet. Chem.* **487** 273 (1995)
229. G Asensio, R Mello, C Boix-Bernardini, M E Gonzalez-Nunez, G Castellano *J. Org. Chem.* **60** 3692 (1995)
230. W Adam, D Reinhardt, H-U Reissing, K Paulini *Tetrahedron* **51** 12257 (1995)
231. W Adam, J Jeko, A Levai, C Nemes, T Patonay, P Sebok *Tetrahedron Lett.* **36** 3669 (1995)
232. W Adam, J Jeko, A Levai, Z Majer, C Nemes, T Patonay, L Parkanyi, P Sebok *Tetrahedron: Asymmetry* **7** 2437 (1996)
233. R Saladino, R Bernini, E Mincione, P Tagliatesta, T Boschi *Tetrahedron Lett.* **37** 2647 (1996)

234. R Saladino, P Lupattelli, E Mincione *Tetrahedron Lett*. **34** 6313 (1993)
235. P E Sonnet, T A Foglia *J. Am. Oil Chem. Soc*. **73** 461 (1996)
236. M Sauter, W Adam *Acc. Chem. Res*. **28** 289 (1995)
237. W Adam, L Hadjiarapoglou, T Mosandl, C R Saha-Möller, D Wild *J. Am. Chem. Soc*. **113** 8005 (1991)
238. W Adam, L Hadjiarapoglou, T Mosandl, C R Saha-Möller, D Wild *Angew. Chem., Int. Ed. Engl*. **30** 200 (1991)
239. W Adam, J Bialas, L Hadjiarapoglou, M Sauter *Chem. Ber*. **125** 231 (1992)
240. W Adam, K Peters, M Sauter *Synthesis* 111 (1994)
241. W Adam, M Sauter *Tetrahedron* **50** 11441 (1994)
242. W Adam, M Sauter *Tetrahedron* **50** 8393 (1994)
243. W Adam, L Hadjiarapoglou, K Peters, M Sauter *J. Am. Chem. Soc*. **115** 8603 (1993)
244. S Oishi, S D Nelson *J. Org. Chem*. **57** 2744 (1992)
245. F Nan, X Chen, Z Xiong, T Li, Y Li *Synth. Commun*. **24** 2319 (1994)
246. J Ashby, B M Elliot, in *Comprehensive Heterocyclic Chemistry* Vol. 1 (Ed. O Methcohn) (Oxford: Pergamon Press, 1984) p. 135
247. M R Boyd *Nature* (*London*) **269** 713 (1971)
248. A G Gonzalez, N L Alvarenga, A Estevez-Braun, A G Ravelo, R Estevez-Reyes *Tetrahedron* **52** 10 667 (1996)
249. W Adam, J Bialas, L Hadjiarapoglou, T Patonay *Synthesis* 49 (1992)
250. W Adam, J Jeko, A Levai, C Nemes, T Patonay *Liebigs Ann. Chem*. 1547 (1995)
251. T Patonay, A Levai, C Nemes, T Timar, G Toth, W Adam *J. Org. Chem*. **61** 5375 (1996)
252. W Adam, D Golsch, L Hadjiarapoglou, T Patonay *Tetrahedron Lett*. **32** 1041 (1991)
253. W Adam, D Golsch, L Hadjiarapoglou, T Patonay *J. Org. Chem*. **56** 7292 (1991)
254. C Nemes, A Levai, T Patonay, G Toth, S Boros, J Halasz, W Adam, D Golsch *J. Org. Chem*. **59** 900 (1994)
255. W Adam, L Hadjiarapoglou, A Levai *Synthesis* 436 (1992)
256. B A Marples, J P Muxworthy, K H Baggaley *Tetrahedron Lett*. **32** 533 (1991)
257. P Bovicelli, P Lupattelli, E Mincione *J. Org. Chem*. **59** 4304 (1994)
258. S W Baertschi, K D Raney, M P Stone, T M Harris *J. Am. Chem. Soc*. **110** 7929 (1988)
259. R Curci, A Detomaso, T Prencipe, G B Carpenter *J. Am. Chem. Soc*. **116** 8112 (1994)
260. R Curci, A Detomaso, M E Lattanzio, G B Carpenter *J. Am. Chem. Soc*. **118** 11089 (1996)
261. A Messeguer, F Sanchez-Baeza, J Casas, B D Hammock *Tetrahedron* **47** 1291 (1991)
262. A-M Lluch, F Sanchez-Baeza, A Messeguer, C Fusco, R Curci *Tetrahedron* **49** 6299 (1993)
263. M Ferrer, F Sanchez-Baeza, A Messeguer, A Diez, M Rubiralta *J. Chem. Soc., Chem. Commun*. 293 (1995)
264. R W Murray, D Gu *J. Chem. Soc., Perkin Trans. 2* 2203 (1993)
265. A L Baumstark, D B Harden *J. Org. Chem*. **58** 7615 (1993)
266. R W Murray, M Singh, B L Williams, H M Moncrieff *Tetrahedron Lett*. **36** 2437 (1995)
267. R W Murray, M Singh, B L Williams, H M Moncrieff *J. Org. Chem*. **61** 1830 (1996)
268. W Adam, A K Smerz *J. Org. Chem*. **61** 3506 (1996)
269. R W Murray, D L Shiang, M Singh *J. Org. Chem*. **56** 3677 (1991)
270. Y Angelis, X Zhang, M Orfanopoulos *Tetrahedron Lett*. **37** 5991 (1996)
271. R G Harvey *Acc. Chem. Res*. **14** 218 (1981)
272. R Mello, F Ciminale, M Fiorentino, C Fusco, T Prencipe, R Curci *Tetrahedron Lett*. **31** 6097 (1990)
273. S K Agarwal, D R Boyd, W B Jennings, R M McGuckin, G A O'Kane *Tetrahedron Lett*. **30** 123 (1989)
274. R W Murray, R Jeyaraman, L Mohan *Tetrahedron Lett*. **27** 2335 (1986)
275. R W Murray, S N Rajadhyaksha, L Mohan *J. Org. Chem*. **54** 5783 (1989)
276. P E Eaton, G E Wicks *J. Org. Chem*. **53** 5353 (1988)
277. R W Murray, M Singh, N Rath *Tetrahedron: Asymmetry* **7** 1611 (1996)
278. M D Wittman, R L Halcomb, S J Danishefsky *J. Org. Chem*. **55** 1981 (1990)
279. J K Crandall, T Reix *J. Org. Chem*. **57** 6759 (1992)
280. G A Olah, Q Liao, C-S Lee, G K Surya Prakash *Synlett* 427 (1993)
281. R W Murray, M Singh *Synth. Commun*. **19** 3509 (1989)
282. R W Murray, M Singh *Tetrahedron Lett*. **29** 4677 (1988)
283. R W Murray, M Singh *Magn. Res. Chem*. **29** 962 (1991)
284. R W Murray, M Singh *J. Org. Chem*. **55** 2954 (1990)
285. M E Brik *Tetrahedron Lett*. **36** 5519 (1995)
286. W Adam, K Briviba, F Duschek, D Golsch, W Kiefer, H Sies *J. Chem. Soc., Chem. Commun*. 1831 (1995)
287. W Adam, C van Barneveld, D Golsch *Tetrahedron* **52** 2377 (1996)
288. A Altamura, R Curci, J O Edwards *J. Org. Chem*. **58** 7289 (1993)
289. P Camps, D Munoz-Torrero, V Munoz-Torrero *Tetrahedron Lett*. **36** 1917 (1995)
290. W Adam, L Hadjiarapoglou *Tetrahedron Lett*. **33** 469 (1992)
291. W Adam, D Golsch, L Hadjiarapoglou, A Levai, C Nemes, T Patonay *Tetrahedron* **50** 13113 (1994)
292. D Curi, V L Pardini, H Viertler, A L Baumstark, D B Harden *Heteroat. Chem*. **5** 555 (1994)
293. C Baldoli, P Del Buttero, E Licandro, S Maiorana, A Papagni *Synlett* 666 (1995)
294. E L Clennan, K L Stensaas *J. Org. Chem*. **61** 7911 (1996)
295. S Colonna, N Gaggero *Tetrahedron Lett*. **30** 6233 (1989)
296. R W Murray, R Jeyaraman, M K Pillay *J. Org. Chem*. **52** 746 (1987)
297. W Adam, W Haas, B B Lohray *J. Am. Chem. Soc*. **113** 6202 (1991)
298. W Adam, D Golsch *Chem. Ber*. **127** 1111 (1994)
299. N Gaggero, L D'Accolti, S Colonna, R Curci *Tetrahedron Lett*. **38** 5559 (1997)
300. G Asensio, R Mello, M E Gonzalez-Nunez *Tetrahedron Lett*. **37** 2299 (1996)
301. A Messeguer *Acros Org. Acta* **1** 71 (1995)
302. W Adam, R M Schuhmann *Liebigs. Ann. Chem*. 635 (1996)
303. W Adam, R M Schuhmann *J. Org. Chem*. **61** 874 (1996)
304. W Adam, J Putterlik, R M Schuhmann, J Sundermeyer *Organometallics* **15** 4586 (1996)
305. W Adam, U Azzena, F Prechtl, K Hindahl, W Malisch *Chem. Ber*. **125** 1409 (1992)
306. W Malisch, M Neumayer, O Fey, W Adam, R Schuhmann *Chem. Ber*. **128** 1257 (1995)
307. E Chelain, R Goumont, L Hamon, A Parlier, M Rudler, H Rudler, J-C Daran, J Vaissermann *J. Am. Chem. Soc*. **114** 8088 (1992)
308. S Sun, J O Edwards, D A Sweigart, L D'Accolti, R Curci *Organometallics* **14** 1545 (1995)
309. W Malisch, K Hindahl, K Gruen, W Adam, F Prechtl, W S Sheldrick *J. Organomet. Chem*. **509** 209 (1996)
310. W A Schenk, J Frisch, W Adam, F Prechtl *Inorg. Chem*. **31** 3329 (1992)
311. W A Schenk, J Frisch, W Adam, F Prechtl *Angew. Chem., Int. Ed. Engl*. **33** 1609 (1994)
312. W A Schenk, J Frisch, M Duerr, N Burzlaff, D Stalke, R Fleischer, W Adam, F Prechtl, A K Smerz *Inorg. Chem*. **36** 2372 (1997)
313. P W N Christian, R Gil, K Muniz-Fernandez, S E Thomas, A T Wierzchleyski *J. Chem. Soc., Chem. Commun*. 1569 (1994)
314. A M Lluch, F Sanchez-Baeza, F Camps, A Messeguer *Tetrahedron Lett*. **32** 5629 (1991)
315. A M Lluch, L Jordi, F Sanchez-Baeza, S Ricart, F Camps, A Messeguer, J M Moreto *Tetrahedron Lett*. **33** 3021 (1992)
316. J Barluenga, R-M Canteli, J Florez, S Garcia-Granda, A Gutierrez-Rodriguez *J. Am. Chem. Soc*. **116** 6949 (1994)
317. A M Lluch, M Gibert, F Sanchez-Baeza, A Messeguer *Tetrahedron* **52** 3973 (1996)
318. A M Lluch, L Jordi, F Sanchez-Baeza, S Ricart, F Camps, J M Moreto, A Messeguer *An. Quim*. **90** 407 (1994)
319. W Adam, M Muller, F Prechtl *J. Org. Chem*. **59** 2358 (1994)
320. W Adam, F Prechtl *Chem. Ber*. **127** 667 (1994)
321. W Adam, G Asensio, R Curci, M E Gonzalez-Nunez, R Mello *J. Am. Chem. Soc*. **114** 8345 (1992)
322. R W Murray, M K Pillay, R Jeyaraman *J. Org. Chem*. **53** 3007 (1988)
323. R W Murray, M K Pillay *Tetrahedron Lett*. **29** 15 (1988)

324. M Cantos, M Merchan, F Tomas-Vert, B O Roos *Chem. Phys. Lett.* **229** 181 (1994)
325. V Y Elemes, S K Silverman, C Sheu, M Kao, C S Foote, M M Alvarez, R L Whetten *Angew. Chem.* **104** 364 (1992)
326. E M Pearch, T K Kwei, S Lu *Polym. Mater. Sci. Eng.* **75** 178 (1996)
327. WO PCT 91 12 369; *Chem. Abstr.* 210 522 (1990)
328. T J McDonough, A Marquis, A J Ragauskas, in *International Pulp Bleached Conference (Abstracts of Reports), Vancouver, 1994* p. 47
329. D Santiago, A Rodriguez, J Szwec, A L Baumstark, A J Ragauskas *Ind. Eng. Chem. Res.* **34** 400 (1995)
330. K Hunt, C L Lee *J. Pulp Pap. Sci.* **21** J263 (1995)
331. K G McGrouther, R W Allison *Appita J.* **48** 445 (1995)
332. A J Ragauskas *Adv. Oxygen. Proc.* **4** 177 (1995)
333. Y Sun, D S Argyzopoulos *Holzforschung* **50** 175 (1996)
334. W A Herrmann, R W Fischer, D W Marz *Angew. Chem., Int. Ed. Engl.* **30** 1638 (1991)
335. S Yamazaki, J H Espenson, P Huston *Inorg. Chem.* **32** 4683 (1993)
336. W A Herrmann, R W Fischer, W Scherer, M U Rauch *Angew. Chem., Int. Ed. Engl.* **32** 1157 (1993)
337. W Adam, W A Herrmann, J Lin, C R Saha-Möller, R W Fischer, J D G Correia *Angew. Chem., Int. Ed. Engl.* **33** 2475 (1994)
338. A M Al-Ajlouni, J H Espenson *J. Org. Chem.* **61** 3969 (1996)
339. R W Murray, K Iyanar, J Chen, J T Wearing *Tetrahedron Lett.* **36** 6415 (1995)
340. R W Murray, K Iyanar, J Chen, J T Wearing *Tetrahedron Lett.* **37** 805 (1996)
341. W Adam, R Curci *Chim. Ind. (Milan)* **63** 20 (1981)
342. N J Turro, H-C Steinmetzer, A Yekta *J. Am. Chem. Soc.* **95** 6470 (1973)
343. V P Kazakov, D V Kazakov, A I Voloshin, N N Kabal'nova, V V Shereshovets *Khimiya i Khemilyuminestsentsiya Dioksiranov* (The Chemistry and Chemiluminescence of Dioxiranes) (Moscow: Nauka, 1999)
344. V A Belyakov, R F Vasil'ev, in *Molekulyarnaya Fotonika* (Molecular Photonics) (Leningrad: Nauka, 1970)
345. R F Vasil'ev *Nature* (*London*) **196** 668 (1962)
346. V A Belyakov, R F Vasil'ev *Photochem. Photobiol.* **11** 179 (1979)
347. R F Vasil'ev *Progr. React. Kinet.* **4** 305 (1967)
348. V Ya Shlyapintokh, O N Karpukhin, L M Postnikov, I V Zakharov, A A Vichutinskii, V F Tsepalov *Khemilyuminestsentnye Metody Issledovaniya Medlennykh Khimicheskikh Protsessov* (Chemiluminescence Methods of Investigation of Slow Chemical Processes) (Moscow: Nauka, 1966)
349. T Wilson, A P Schaap *J. Am. Chem. Soc.* **93** 4126 (1971)
350. H-C Steinmetzer, P Lechtken, N J Turro *Liebigs. Ann. Chem.* 1984 (1973)
351. W Adam, E Cancio, O Rodriguez *Photochem. Photobiol.* **27** 617 (1978)
352. P Lechtken, N J Turro *Mol. Photochem.* **6** 95 (1974)
353. G A Tolstikov, G L Sharipov, A I Voloshin, S S Ostakhov, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Khim.* 787 (1986) [a]
354. G L Sharipov, V P Kazakov, G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Phys.* **51** 559 (1987)
355. S S Ostakhov, G L Sharipov, A I Voloshin, V P Kazakov, G A Tolstikov *Dokl. Akad. Nauk SSSR* **287** 1165 (1986) [c]
356. G L Sharipov, A I Voloshin, S S Ostakhov, V P Kazakov, G A Tolstikov *Khimicheski Initsiirovannaya Elektronoobmennaya Lyuminestsentsiya pri Kataliticheskoi Aktivatsii Razlozheniya Dioksetanov Dipiridil'nym Kompleksom Dvukhvalentnogo Ruteniya* [Chemically Initiated Electron Exchange Luminescence at Catalytic Activation of Decomposition of Dioxetanes by Dipyridyl Complex of Bivalent Ruthenium (Preprint)] (Ufa: Institute of Chemistry, Bashkiriya Scientific Centre, Ural Branch of Academy of Science of the USSR, 1989)
357. A I Voloshin, G L Sharipov, V P Kazakov, G A Tolstikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1316 (1991) [a]
358. G J Kavarnos, N J Turro *Chem. Rev.* **86** 401 (1986)
359. S S Miller, K Zahir, A Haim *Inorg. Chem.* **24** 3978 (1985)
360. C S Foote *Acc. Chem. Res.* **1** 104 (1968)
361. K Gollnick, in *Singlet Oxygen Reactions with Organic Compounds and Polymers* (Eds B Ranby, J F Rabek) (New York: Wiley, 1978) p. 111
362. B M Monroe, in *Singlet Oxygen* Vol. 1 (Ed. A A Frimer) (Boca Raton, FL: CRC Press, 1985)
363. A Lange, H-D Brauer *J. Chem. Soc., Perkin Trans. 2* 805 (1996)
364. D F Evans, M W Upton *J. Chem. Soc., Dalton Trans.* 1151 (1985)
365. K Briviba, C R Saha-Möller, W Adam, H Sies *Biochem. Mol. Biol. Int.* **38** 647 (1996)
366. V I Vedeneev, A E Shilov *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Modern Problems) (Moscow: Khimiya, 1985)
367. P Lechtken, A Yekta, N J Turro *J. Am. Chem. Soc.* **95** 3028 (1973)
368. N J Turro, N E Schore, H-C Steinmetzer, A Yekta *J. Am. Chem. Soc.* **96** 1938 (1974)
369. N J Turro, P Lechtken, N E Schore, G Schuster, H-C Steinmetzer, A Yekta *Acc. Chem. Res.* **7** 97 (1974)
370. N J Turro, G B Schuster, J Pouliquen, R Petit, C Mauldin *J. Am. Chem. Soc.* **96** 6799 (1974)
371. A I Voloshin, G L Sharipov, V P Kazakov, G A Tolstikov *Dokl. Akad. Nauk SSSR* **297** 368 (1987) [c]
372. R G Bulgakov, G Ya Maistrenko, V N Yakovlev, S P Kuleshov, G A Tolstikov, V P Kazakov *Dokl. Akad. Nauk SSSR* **282** 1385 (1985) [c]
373. R G Bulgakov, V P Kazakov, G A Tolstikov *J. Organomet. Chem.* **387** 11 (1990)
374. R G Bulgakov, V P Kazakov, G A Tolstikov *Khemilyuminestsentsiya Metalloorganicheskikh Soedinenii* (Chemiluminescence of Organometallic Compounds) (Moscow: Nauka, 1989)
375. V P Kazakov *Khemilyuminestsentsiya Uranila, Lantanoidov i d-Elementov* (Chemiluminescence of Uranyl, Lanthanides and *d*-Elements) (Moscow: Nauka, 1980)
376. V P Kazakov *Zh. Fiz. Khim.* **39** 2936 (1965) [d]
377. V P Kazakov, Yu K Gusev, G S Parshin, L A Khamidullina *Izv. Akad. Nauk SSSR, Ser. Khim.* 2634 (1977) [a]
378. V P Kazakov, R G Bulgakov *Radiokhimiya* **20** 102 (1978) [e]
379. V P Kazakov, G S Parshin, Yu K Gusev, S V Lotnik, S V Zemskov *Dokl. Akad. Nauk SSSR* **239** 1397 (1978) [c]
380. V P Kazakov, G S Parshin, R G Bulgakov, L A Khamidullina, D D Afonichev *Radiokhimiya* **21** 199 (1979) [e]
381. Yu K Gusev, V P Kazakov, L A Khamidullina, S V Lotnik, S V Zemskov, in *Khimiya Urana* (The Chemistry of Uranium) (Moscow: Nauka, 1981) p. 264
382. A V Mamykin, G S Parshin, V P Kazakov *Zh. Fiz. Khim.* **58** 464 (1984) [d]
383. A D Karavaev, V P Kazakov *Radiokhimiya* **27** 570 (1985) [e]
384. V P Kazakov, D D Afonichev, L A Khamidullina, S P Kuleshov *Radiokhimiya* **29** 165 (1987) [e]
385. S V Lotnik, V M Kalinina, V P Kazakov, G A Tolstikov *Dokl. Akad. Nauk SSSR* **296** 918 (1987) [c]
386. V A Antipin, G S Parshin, V P Kazakov, S N Zagidullin *React. Kinet. Catal. Lett.* **27** 103 (1985)
387. A I Voloshin, G L Sharipov, V P Kazakov, G A Tolstikov *Izv. Akad. Nauk, Ser. Khim.* 1056 (1992) [a]
388. N Sh Ableeva, A I Voloshin, E V Vasil'eva, G L Sharipov, L M Khalilov, V P Kazakov *Kinet. Katal.* **34** 811 (1993) [b]
389. G L Sharipov, S S Ostakhov, N Sh Ableeva, A I Voloshin, V P Kazakov, G A Tolstikov *Izv. Akad. Nauk, Ser. Khim.* 1824 (1993) [a]
390. N Sh Ableeva, A I Voloshin, S S Ostakhov, A G Kukovinets, V N Korobeinikova, V P Kazakov, G A Tolstikov *Izv. Akad. Nauk, Ser. Khim.* 1762 (1994) [a]
391. V P Kazakov, A I Voloshin, V A Antipin, I A Khusainova *Izv. Akad. Nauk, Ser. Khim.* 1844 (1995) [a]
392. V A Antipin, A I Voloshin, S S Ostakhov, V P Kazakov *Izv. Akad. Nauk, Ser. Khim.* 1159 (1996) [a]
393. V P Kazakov, A I Voloshin, S S Ostakhov, I A Khusainova *Izv. Akad. Nauk, Ser. Khim.* 2479 (1996) [a]
394. V P Kazakov, A I Voloshin, S S Ostakhov, N Sh Ableeva *Khim. Vys. Energ.* **30** 295 (1996) [f]
395. N Sh Ableeva, A I Voloshin, S S Ostakhov, V P Kazakov, G A Tolstikov *Khim. Fiz.* **15** 34 (1996) [g]
396. V P Kazakov, A I Voloshin, S S Ostakhov, N Sh Ableeva *Khim. Vys. Energ.* **31** 129 (1997) [f]
397. V P Kazakov, A I Voloshin, S S Ostakhov, I A Khusainova, E V Zharinova *Izv. Akad. Nauk, Ser. Khim.* 724 (1997) [a]
398. V P Kazakov, A I Voloshin, S S Ostakhov, I A Khusainova, E V Zharinova *Izv. Akad. Nauk, Ser. Khim.* 730 (1997) [a]

399. V P Kazakov, A I Voloshin, S S Ostakhov *Opt. Spektrosk.* **83** 860 (1997) [h]
400. V P Kazakov, A I Voloshin, S S Ostakhov, N Sh Ableeva *Khim. Vys. Energ.* **30** 456 (1996) [f]
401. V P Kazakov, A I Voloshin, S S Ostakhov *Dokl. Akad. Nauk* **354** 65 (1997) [c]

[a] — *Russ. Bull. Chem. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*
[c] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[d] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[e] — *Radiochemistry (Engl. Transl.)*
[f] — *High Energy Chem. (Engl. Transl.)*
[g] — *Russ. J. Chem. Phys. (Engl. Transl.)*
[h] — *Opt. Spectrosc. (Engl. Transl.)*