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SINGLET OXYGEN PHOTOOXYGENATION OF FURANS

ISOLATION AND REACTIONS OF (4+2)-CYCLOADDITION PRODUCTS (UNSATURATED SEC.-OZONIDES)

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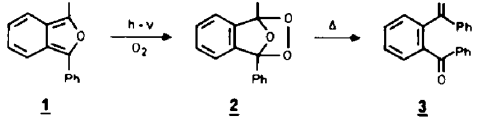
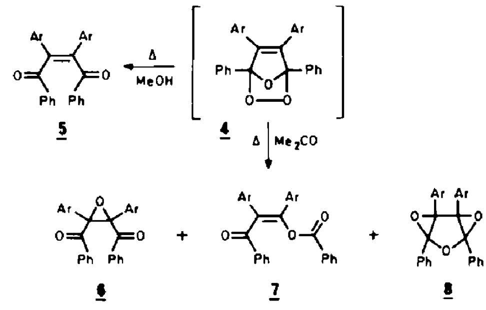
Abstract—Tetraphenylporphin-photosensitized oxygenations of furan (**19**), 2-methylfuran (**26**), 2-ethylfuran (**39**), furfurylalcohol (**24**), 2-acetylfuran (**40**), 2-methoxyfuran (**42**), 2,5-dimethylfuran (**30**), furfural (**25**) and 5-methylfurfural (**41**) in non-polar aprotic solvents yield the corresponding monomeric unsaturated secondary ozonides due to a (4+2)-cycloaddition of singlet oxygen to these furans. With the exception of the ozonide derived from **25**, the ozonides were isolated and characterized (^{1}H- and ^{13}C-NMR spectra, etc.). In non-polar aprotic solvents, the ozonides derived from **19**, **26** and **39** undergo thermal rearrangements to the corresponding *cis*-diepoxides and epoxylactones. Ozonide **31**, derived from **30**, however, dimerizes; only above about 60° is a *cis*-diepoxide formed from either **31** or its dimer. Rose bengal-photosensitized oxygenations of the furans in alcohols (MeOH, EtOH, i-PrOH) also produce the corresponding ozonides as the primary products of (4+2)-cycloadditions of singlet oxygen to these furans. However, reactions of the alcohols with the ozonides are too fast to allow the ozonides to be isolated. Instead, the same products are obtained as are isolated from reactions carried out by dissolving the ozonides in the alcohols. Depending on the structure of the ozonide, three pathways are available to ozonide/alcohol (ROH) interactions: (1) addition of ROH to yield alkoxy hydroperoxides; one out of several possible isomers is formed in a completely stereoselective and regiospecific reaction; (2) elimination of a bridgehead proton by ROH as a base, as observed with the ozonide derived from **19** to give hydroxy butenolide (**78**) in yields between 20 and 60%; and (3) ROH-attack on a carbonyl side-chain under elimination of the corresponding alkyl ester, as observed with furfural photooxygenation which yielded hydroxy butenolide (**78**) in high yields (> 95%). Interaction of ozonide **31** with tert.-butyl alcohol (t-BuOH) yields quantitatively *cis*-3-oxo-1-butenylacetate (**81**) by a Baeyer–Villiger-type rearrangement with vinyl group migration. Hydrogen-bonding between the alcohol and the peroxy group of the ozonides assist the heterolysis of the C—O bonds in the ozonides; the most stabilized cation develops. Front-attack of ROH on this cation explains the stereoselectivity as well as the regiospecificity of the alkoxy hydroperoxide formation; with a bulky alcohol like t-BuOH, ROH-attack on the cation is sterically hindered thus allowing a rearrangement to occur. 1,3-Dipolar cycloaddition of *p*-nitrophenyl azide to ozonide **31** proceeds stereoselectively to one of the isomers **87a**/**87b**. Finally, kinetic results of furan photooxygenation in methanol show the following order of furan-reactivity towards singlet oxygen: **30** > **42** > **26** > **19** > **41** > **25**, with absolute rate constants ranging from 1.8×10^8 (with **30**) to 8.4×10^4 M^{-1} s^{-1} (with **25**).

In 1944, Schenck[1] postulated that furan-endoperoxides (= ozonides) should be formed as instable primary products when furans are subjected to sensitized or auto-sensitized photooxygenations. Two years later, Dufraisse and Ecary[2] succeeded in isolating an explosive product from 1,3-diphenylisobenzofuran (**1**), for which the structure of an ozonide (**2**) was suggested. In substance, ozonide **2** exploded at 18°; in solution it underwent a decomposition reaction to give *o*-dibenzoylbenzene (**3**).



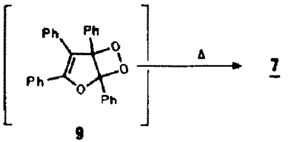
In 1960, Wasserman and Liberles[3] described some solvent-dependent transformations of the photooxygenation product, obtained from tetraphenylfuran and assumed to be the ozonide **4a**.



a: Ar = Ph
b: Ar = p-Br-C_6H_4

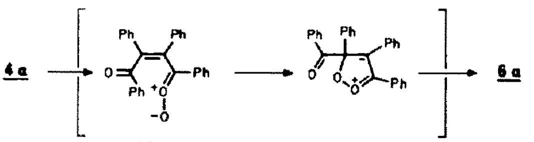
Thus, when tetraphenylfuran was irradiated in oxygen-containing methanol in the presence of methylene blue as a sensitizer, *cis*-dibenzoylstilbene (**5a**) was isolated; if the reaction was carried out in acetone, the oxirane derivative **6a** and the enolbenzoate **7a** were obtained. Similar observations were made by Lutz *et al.*[4] in 1962, who showed that photooxygenation of 2,5-diphenyl-3,4-di-*p*-bromophenylfuran in acetone resulted in the formation of an oxirane (**6b**) and an enolbenzoate (**7b**); however, the main product was the diepoxide **8b**.

Wasserman and Liberles[3] explained the formation of **7** as occurring by a Baeyer–Villiger-type rearrangement of **4**, whereas LeRoux and Basselier[5] assumed that a 1,2-dioxetane (**9**) rather than an ozonide (**4**) is formed during the photooxygenation reaction; **9** should suffer the usual cleavage to carbonyl compounds, in this case to the enolbenzoate **7**.



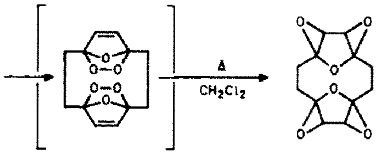
9

In 1975, Wasserman and Saito[6] showed that oxirane **6** was formed nearly quantitatively when tetraphenylfuran was irradiated in aqueous tetrahydrofuran in the presence of a sensitizer and oxygen. A rearrangement of **4a** to give an intermediate carbonyl-oxide **10a** followed by ring closure to **10b** and a further rearrangement to **6a** was discussed. Evidence for the carbonyl-oxide intermediate was provided by trapping **10a** with diphenylsulfide yielding **5a** and diphenylsulfoxide.[6]



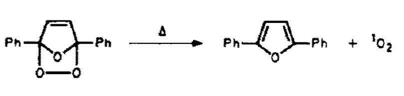
10a **10b**

A similar rearrangement to that observed by Lutz *et al.*[4] (**4b** → **8b**) was reported by Wasserman[7] in 1970: the bis-ozonide **11**, assumed to be formed as the primary instable product from the corresponding furanophane, underwent a rearrangement in methylene chloride to bis-diepoxide **12**.



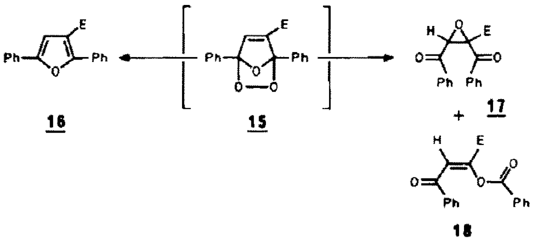
11 **12**

In 1967, Dufraisse *et al.*[8] showed that the ozonide **13** obtained from 2,5-diphenylfuran (**14**) undergoes a retro-(4 + 2)-cycloaddition reaction to yield furan **14** and molecular oxygen. That this oxygen is eliminated as singlet oxygen was shown by Trozzolo and Fahrenholtz[9] in 1970 by trapping $^1O_2$ with 1,3-cyclohexadiene as well as with rubrene.



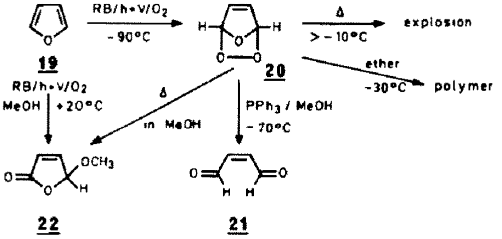
13 **14**

More recently, Graziano *et al.*[10,11] studied the behavior of electron-acceptor substituted ozonides (**15**) in non-polar aprotic solvents, showing that the main reactions are retro-(4 + 2)-cycloadditions to **16** as well as rearrangements to oxiranes (**17**) and enolbenzoates (**18**).



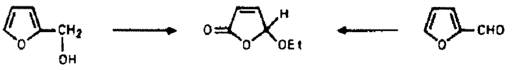
16 **15** + **17** **18**

Schenck[1,12] studied the photosensitized oxygenation of furan and a series of alkyl-substituted furans. When furan (**19**) was irradiated in the presence of oxygen and rose bengal (RB) as a sensitizer in a 2:2:1 mixture of MeOH–EtOH–Me_2CO at −90°, Koch and Schenck[13] isolated a product which exploded at about −10°; it was reduced to maleic dialdehyde (**21**) in ether at −70°, and it was transformed into the pseudo-methylester of *cis*-β-formylacrylic acid (= 4-methoxybutenolide; **22**) if treated with methanol. Butenolide **22** could be obtained directly, if **19** was photooxygenated in MeOH at room temp. The most likely structure of the instable peroxidic product is that of the ozonide **20**.



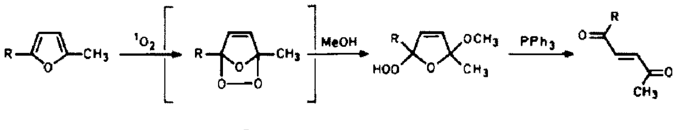
19 **20** **22** **21**

Butenolide **23** was obtained when furfuryl alcohol (**24**)[14] and furfural (**25**)[15,16] were subjected to photosensitized oxygenations in ethanol.

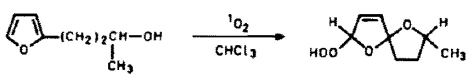


24 **23** **25**

The formation of butenolides was assumed to occur via the corresponding instable ozonides and alkoxyhydroperoxides since Schenck and Schulte-Elte[17] succeeded in isolating the latter from 2-methylfuran (**26**)[17] and 2,5-dimethylfuran (**30**).[17,18] Similarly, when



26 R = H **27** **28** **29**
30 R = CH_3 **31** **32** **33**



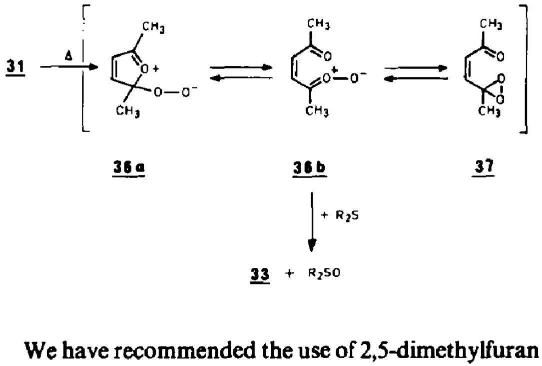
34 **35**

2-(3-hydroxybutyl)furan (**34**) was photooxygenated in $CHCl_3$, spiro compound **35** was obtained.[19]

Reduction of **28** and **32** as well as of **27** and **31** prepared in non-alcoholic solvents yielded the unsaturated 1,4-dicarbonyl compounds **29** and **33**, respectively. On standing, the non-alcoholic solution of **31** gave rise to an isolable dimer.[18]

Recently, Adam and Takayama[20] tried to isolate ozonide **31** by irradiating **30** in CCl_4 at 0° in the presence of tetraphenyl porphyrin and oxygen followed by removal of the solvent by flash distillation at $-20°/0.1$ Torr. They obtained a co-distillation of **31** and CCl_4 and observed ^{1}H-NMR signals at δ 6.02 and 1.70 (in CCl_4) which they attributed to the two olefinic protons and the 6 protons of the 2 Me groups of **31**, respectively. Graziano *et al.*[10] also reported on **31** in CCl_4; in this case, the chemical shifts were observed at δ 6.20 and 1.75 (in CCl_4). These signals probably belong to the dimer of **31** (= **38**) rather than to the monomeric ozonide **31** (see ref. 27 and below). Feringa[21] reported on the ^{1}H-NMR spectrum of **31** in $CDCl_3$, with signals at δ 6.38 (2 olefinic H) and 1.82 (2 Me-groups). These signals, however, certainly belong to the dimer of **31** (see below).

As described above, ozonides such as **2** suffer a thermal decomposition to 1,2-diacylbenzene (or, more generally, to a 1,2-diacylethylene, see **4** → **5**, **15** → **16**). The fate of the O atom that is lost during the reaction remained obscure. Wasserman[6] as well as Adam and Rodriguez[22] showed recently that an O atom may be transferred to suitable acceptors such as ethylenes, sulfides and ketones to yield oxiranes, sulfoxides and esters (by a Baeyer–Villiger oxidation), respectively. Adam[22] concluded that the O-transfer occurred from an intermediate carbonyl-oxide (**36**) rather than from an instable dioxirane (**37**).

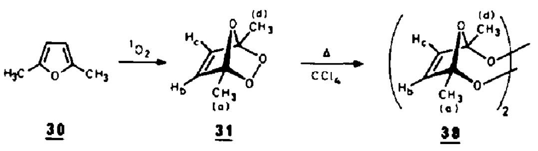


We have recommended the use of 2,5-dimethylfuran (**30**) as a standard singlet oxygen acceptor in methanolic solution in order to determine the limiting (or maximum) quantum yield of singlet oxygen formation from a given sensitizer in MeOH.[23,24] More recently, we studied the solvent-dependence of various olefins and used **30** as a standard singlet oxygen acceptor to determine the limiting rate of singlet oxygen consumption.[25,26] It was, therefore, necessary to study the primary product of singlet oxygen with **30** in a series of solvents, especially its subsequent thermal reactions, in order to assure that these thermal reactions do not interfere with the singlet oxygen reaction. The isolation of ozonide **31** and its subsequent thermal reactions were published recently;[27a] these results will be discussed below in more detail together with our studies on furan (**19**), 2-methylfuran (**26**), 2-ethylfuran (**39**), 2-(hydroxymethyl)furan (**24**), 2-acetylfuran (**40**), 2-methoxyfuran (**42**), furfural (**25**) and 5-methylfurfural (**41**).

RESULTS AND DISCUSSION

1. *Preparation and isolation of ozonides of furan and substituted furans*

2,5-Dimethylfuran (**30**) consumes one molecule of oxygen when irradiated in oxygen-saturated aprotic solvents in the presence of typical singlet oxygen sensitizers such as tetraphenylporphin (TPP) (in CCl_4, $CHCl_3$, $CFCl_3$, CH_2Cl_2 and benzene) and rose bengal (RB) (in Me_2CO and acetonitrile) at 13°. Ozonide **31** was isolated by removing the solvent at low temps and reduced pressure (e.g. $CFCl_3$ at $-15°/0.1$ Torr) followed by distillation of the remaining yellow oil at $5°/10^{-3}$ Torr into a trap cooled to $-78°$.

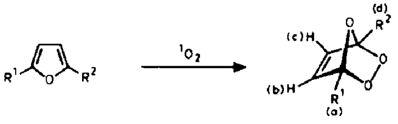


The ^{1}H-NMR spectrum (in $CDCl_3$; TMS) of **31** shows a singlet at δ 6.25 (H_b, H_c) and another singlet at 1.70 ($3H_a$, $3H_d$). The elemental analysis and the molecular weight determination are in accord with the structure of a monomeric ozonide **31**. At low temperature ($< -15°$), small amounts ($<$ 100 mg) of **31** could be stored for several days; larger amounts ($>$ 100 mg) of **31** had always the tendency to decompose violently (explosion!). In CCl_4 and $CFCl_3$, **31** dimerized slowly to peroxide **38**; in benzene–petrol ether (2:1), the dimerization occurs more rapidly. At about 55–60°, the dimerization is fast and quantitative. Compound **38** is a yellowish crystalline compound which decomposes at 143°. Its ^{1}H-NMR spectrum shows two singlets at δ 6.31 (H_b, H_c) and 1.81 ($3H_a$, $3H_d$). The elemental analysis and the molecular weight determination are in accord with a dimer of **31**; the ^{1}H-NMR spectrum shows that the dimer has structure **38**.

Under similar conditions, photooxygenation of furan (**19**) and furan derivatives **24**, **26** and **39**–**42** gave rise to ozonides (Table 1), which were isolated in substance in the cases of ozonide **20** (a crystalline compound which decomposes at about $-15°$) and the substituted ozonides **43** (crystalline, decomposition at about $-20°$), **45** (crystalline, decomposition at about $-40°$), and **27**, **44** and **46** (oils). Ozonide **47** was only obtained in $CFCl_3$ solution; ozonide **48** from furfural (**25**), however, could not be obtained due to its rather slow formation on the one hand and its very fast rearrangement (see below) on the other hand.

With 2,5-dimethylfuran (**30**), we observed the production of a monomeric ozonide (**31**) which underwent dimerization to **38**. The ozonides obtained from the other furans of Table 1 do not show such a dimerization reaction under similar conditions. Since we could not execute molecular weight determinations at low temps (note that decomposition occurred at temps below $-15°$), the products obtained might be the dimers of the ozonides rather than the monomeric ozonides. The ^{1}H-NMR spectra do not allow to decide this question, since we should assume that

Table 1. ^{1}H-NMR spectra of monomeric ozonides



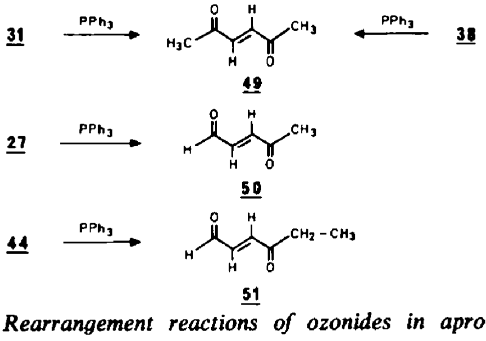
R^1	R^2		H_a	H_b/H_c	H_d
H_a	H_d	**20**	6.38 (s)	6.24 (s)	6.38 (s)
H_a	CH_2OH (d)	**43**		6.62 (m)*	4.30 (m)
H_a	CH_3 (d)	**27**	6.31 (m)	6.15 (m)	1.79 (s)
CH_3 (a)	CH_3 (d)	**31**	1.70 (s)	6.25 (s)	1.70 (s)
H_a	CH_2CH_3 (e) (d)	**44**		6.40 (m)*	e : 2.20 (q) d : 1.17 (t)
H_a	$C(=O)-CH_3$ (d)	**45**	6.73 (m)	6.83 (m)	2.54 (s)
CH_3 (a)	CHO (d)	**46**	1.98 (s)	6.50 (d, J = 5.6) 6.77 (d, J = 5.6)	9.83 (s)
H_a	OCH_3 (d)	**47**		6.05 (m)*	3.72 (s)
H_a	CHO (d)	**48**	—	—	—

* $(H_a + H_b + H_c)$.

monomeric and dimeric ozonides show very similar spectra (see **31** and **38**). However, one would expect that the dimers are more stable: dimer **38** has a m.p. of 143° (dec), and it seems rather unlikely that, for example, the replacement of one Me group by a H atom (giving the dimer of ozonide **27**) should result in destabilizing the dimer to such an extent that it decomposes at room temp. We believe, therefore, that we are dealing with the monomeric ozonides.

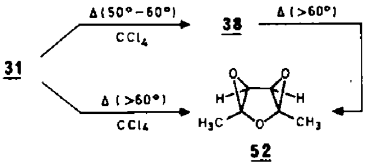
Why, then, do not all the ozonides form dimers? Obviously, if the bridgehead positions of the monomeric ozonides carry a H-atom or a "leaving group" such as CHO (as in **46**), monomolecular reactions (for example, rearrangements) become much faster than the bimolecular dimerization reaction. Only if both bridgehead positions carry rather "inert" substituents (such as Me groups as in **31**) become rearrangements slow enough to allow bimolecular dimerization processes to compete.

Reduction of ozonide **31** in benzene at 0° with an ice-cold solution of triphenylphosphane in petrol ether results in the formation of *trans*-3-hexene-2,5-dione (**49**). This dione is also formed if dimer **38** is reduced under these conditions. Similarly, ozonides **27** and **44** may be reduced to *trans*-acetylacrolein (**50**) and *trans*-propionylacrolein (**51**), respectively.



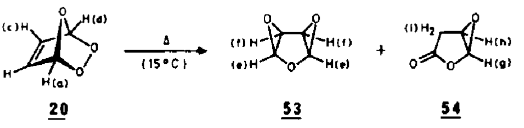
2. *Rearrangement reactions of ozonides in aprotic solvents*

Formation of diepoxides and epoxylactones. If ozonide **31** is slowly heated in CCl_4 to about 55–60°, it dimerizes to **38**. If, however, **31** is rapidly heated to temps above 60° (but distinctly below the reflux temp of CCl_4) it rearranges to diepoxide **52**. This diepoxide is also obtained, if dimer **38** is heated to temps above 60° in CCl_4.



Diepoxide **52** is isolated by distillation at 10°/ < 10^{-4} Torr as a colorless liquid which becomes resinous at room temp within a few hours. The ^{1}H-NMR spectrum of **52** shows two singlets at δ 3.42 (2 tert. H) and 1.58 (2 Me groups). Because of its tendency to turn resinous, heating of **31** to produce **52** should be rather rapid; otherwise, larger amounts of resinous material will accompany the formation of the diepoxide.

If ozonide **20** is kept in CCl_4, $CHCl_3$ or CH_2Cl_2 at room temp for about 30 to 60 min, it rearranges completely to a mixture of diepoxide **53** and epoxylactone **54**.[38]



	53	**54**
In CCl_4:	83%	17%
in $CHCl_3$:	76%	24%
in CH_2Cl_2:	62%	38%

Diepoxide **53** was isolated from CCl_4 solns by sublimation at 70–80°/0.2 Torr as slightly yellowish crystals, m.p. 110–114° (dec), after CCl_4 and epoxylactone **54** were removed by distillation. The epoxylactone **54**, a colorless oil, was obtained from CH_2Cl_2 solution by distillation at 50–55°/0.3 Torr. The structural assignments of **53** as a diepoxide and **54** as an epoxylactone are based on elemental analyses, ^{1}H- and ^{13}C-NMR spectra.

Figure 1 shows the rearrangement of **20** in a 1:3 mixture of $CDCl_3$–$CFCl_3$ at 15°. At the beginning, only the two singlets H_a/H_d at δ 6.38 and H_b/H_c at 6.24 of ozonide **20** (see also Table 1) are present. After 5 min, the appearance of H_e and H_f of diepoxide **53** as singlets at δ

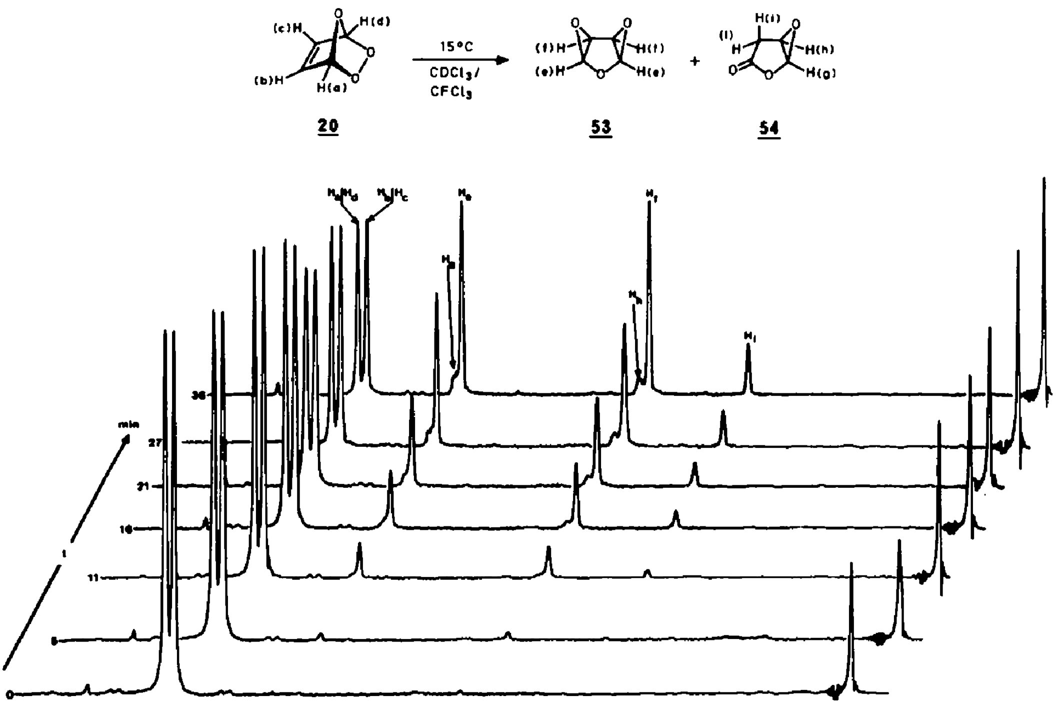
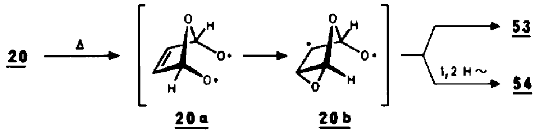


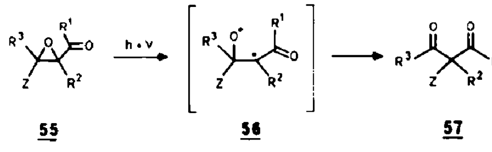
Fig. 1. Rearrangement of ozonide **20** to diepoxide **53** and epoxylactone **54**. ^{1}H-NMR spectra in $CDCl_3$–$CFCl_3$ (1 : 3) at 15°.

5.50 and 3.75, respectively, becomes observable. After another 5 min, the signals of H_g, H_h and H_i of the epoxylactone **54** at δ 5.61, 3.87 and 2.80 start to appear.

The thermal rearrangement reactions of ozonide **20** are quite likely initiated by homolytic cleavage of the O—O bond to yield diradical **20a**. Two-fold ring-closure would yield the *cis*-diepoxide **53**. If the ring-closures occur in two steps, the 1,3-diradical **20b** could be the common intermediate for both products, **53** and **54**. The latter would be formed from **20b** by a 1,2-H shift; increasing solvent polarity appears to favor such shifts.



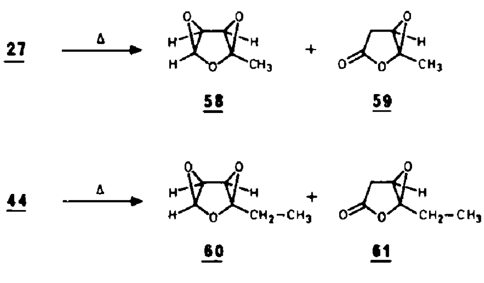
Markos and Reusch[28] have shown that photolysis of epoxy-ketone (**55**) afford 1,3-diketones (**57**), probably via 1,3-diradicals (**56**); the migratory ability decreased in the order Z = Ph_2CH > $PhCH_2$ > H > CH_2R > CH_3. In accord with this order, epoxylactone formation is observed with ozonides **20**, **27** and **44** (see below), but not with ozonide 31.



Ozonides **27** and **44** obtained from 2-methyl- and 2-ethylfuran, **26** and **39**, respectively, rearrange at room temp in CCl_4 within 8–10 hr completely to the corresponding diepoxides (**58** and **60**) (> 90%) and epoxylactones (**59** and **61**) (< 5%).

Distillation of the residues, obtained after removal of CCl_4, at about 10°/ < 10^{-4} Torr into a trap cooled to −78° resulted in colorless oils which represent mixtures of **58**/**59** (9 : 1) and **60**/**61** (3 : 2). The tendency to turn rather rapidly into resinous products prohibited so far the isolation of the pure components. The ^{1}H- and ^{13}C-NMR spectra of the mixtures, taken immediately after distillation, are in accord with structures **58**–**61**.

Ozonides **43** and **45**–**47** (as well as **48** assumed to be the primary product when furfural (**25**) is photooxygenated in aprotic solvents) also undergo rapid thermal reactions in CCl_4 at room temp. We have made no attempt to characterize the resinous material.



3. *Reactions of ozonides with alcohols*

Photooxygenation of furans in alcoholic solutions. If ozonide 31 (or the dimer **38** of ozonide **31**) is treated with alcohols such as MeOH, EtOH and i-PrOH, the 2-alkoxy derivatives **62**–**64** of 2,5-dimethyl-5-hydroperoxy-2,5-dihydrofuran are formed in quantitative yields. The hydroperoxides are more conveniently prepared by irradiating **30** in alcoholic solution in the presence of RB and O_2.

In principle, addition of ROH to **31** may result in the formation of the *cis*- as well as of the *trans*-5-

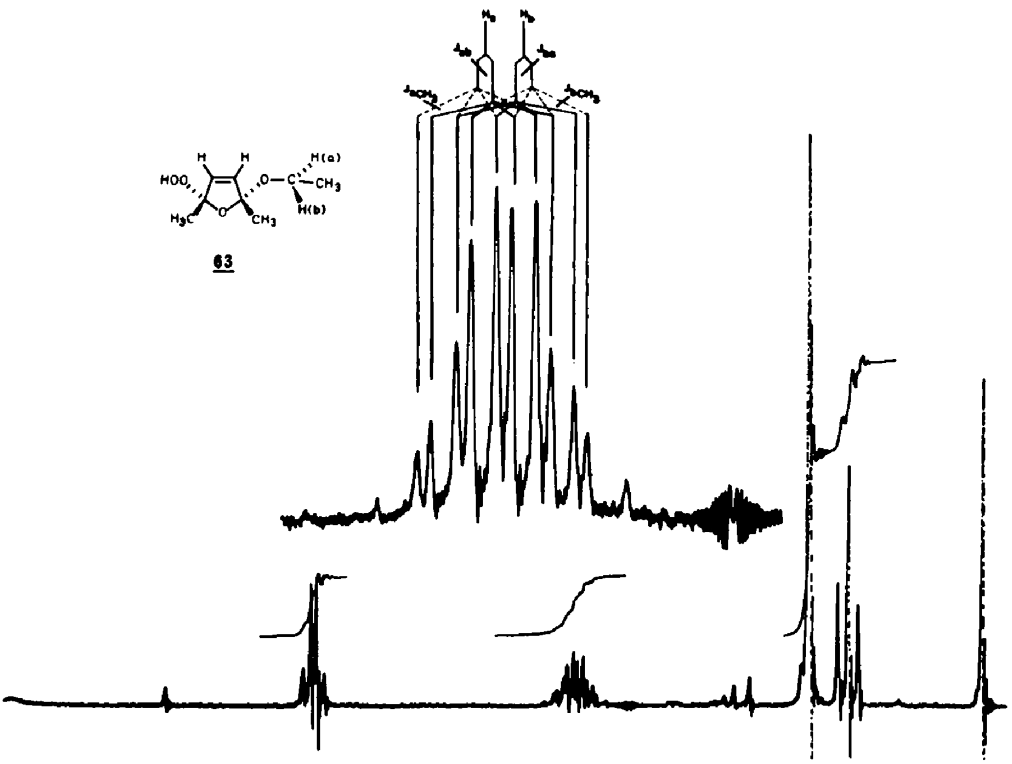
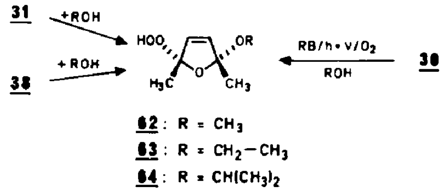
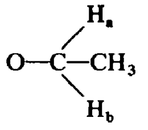


Fig. 2. ^{1}H-NMR spectrum of **63** in $CDCl_3$.



hydroperoxy-2-alkoxy derivative. The proton-decoupled ^{13}C-NMR spectra of **62**–**64** show, however, only one set of ^{13}C-signals in each case, indicating that only one of the steric isomers is formed at a time.

In addition product **63**, the two protons of the methylene group become diastereotopic and should thus give rise to two doublets of quartets. Figure 2 shows the ^{1}H-NMR spectrum of **63**, and the expanded group of signals of the



$$O-\overset{H_a}{\underset{H_b}{C}}-CH_3$$

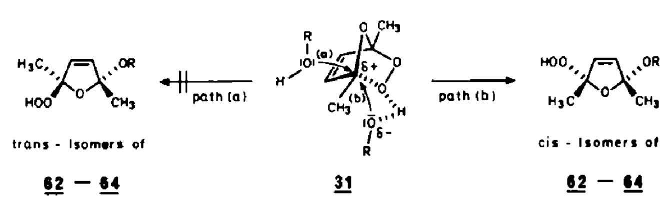
group ($J_{H_a,H_b} = 3$ cps, $J_{H_a,CH_3} = 6.75$ cps, $J_{H_b,CH_3} = 7.25$ cps).

It also shows that **63** represents only one of the steric isomers. (Similar observations are made with compounds **66**, **72** and **75**, see below.)

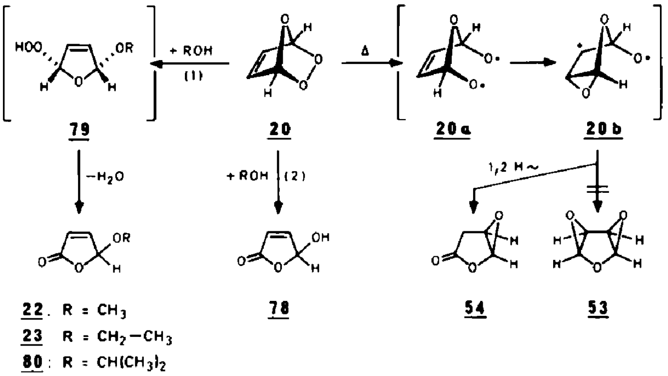
The most likely mechanism of ROH addition to **31** appears to be that of a nucleophilic substitution assisted by the concomitant formation of a H-bonded peroxy group according to Scheme 1.

According to path (a), which we presumed to be the more likely pathway,[27a] **62**–**64** should represent the *trans*-isomers. However, the X-ray structure analysis of **62** revealed that this compound is the *cis*-isomer (*cis*-arrangement of OMe and OOH),[27b] showing that the reaction of **31** with methanol proceeds according to path (b) rather than to path (a). Thus, **63** and **64** should also represent the *cis*-isomers.

Addition of ROH to ozonides **27**, **44** and **47** also results in the formation of only one alkoxy hydroperoxide at a time, although four isomeric addition products could, in principle, be formed in each case. However, ROH-addition is not only entirely stereoselective, it is also regiospecific. Treatment of **65**–**67** with vanadium pentoxide in alcohol gives rise to the exclusive formation of the dehydration products, the butenolides **68**–**70**. This result, together with the observation that the proton-decoupled ^{13}C-NMR

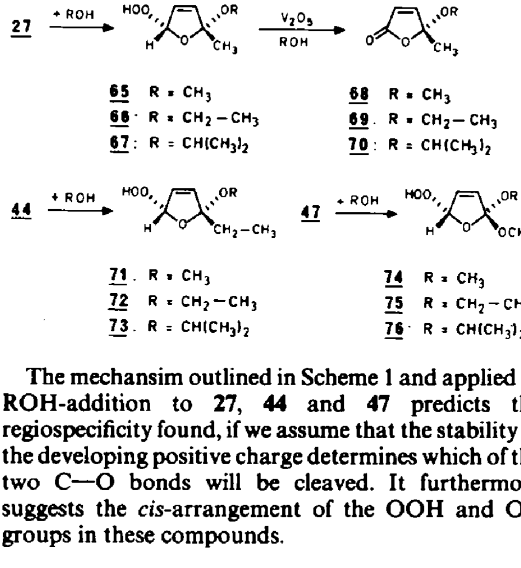


Scheme 1.



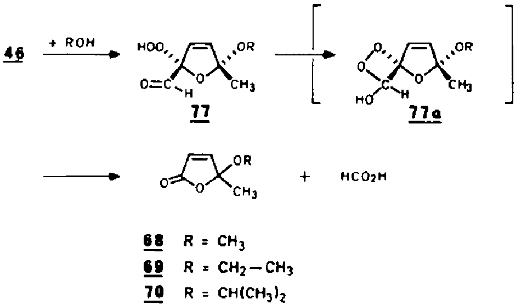
Scheme 2.

spectra of all the alkoxy hydroperoxides prepared show only one set of ^{13}C-signals, is in accord with structures **65–67** from **27**, **71–73** from **44**, and **74–76** from **47**.



The mechansim outlined in Scheme 1 and applied to ROH-addition to **27**, **44** and **47** predicts the regiospecificity found, if we assume that the stability of the developing positive charge determines which of the two C—O bonds will be cleaved. It furthermore suggests the *cis*-arrangement of the OOH and OR groups in these compounds.

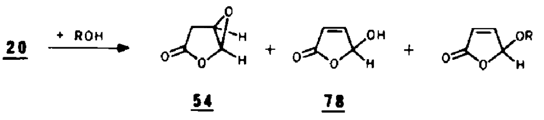
If ozonide **46** is treated with ROH (or if 5-methylfurfural (**41**) is photooxygenated in ROH), alkoxy butenolides **68–70** and formic acid are obtained. According to the mechanism discussed above, alkoxy hydroperoxide **77** is the expected primary product of the ozonide/ROH interaction; in the case of methanol as a solvent, the methoxy-hydroperoxide **77** (R = Me) was detected by ^{1}H-NMR spectroscopy at low temp. Elimination of formic acid from **77** (R = Me) yields **68**, possibly via intermediate **77a**.



Addition of ROH to ozonide **20** in $CHCl_3$ at −20° (or photooxygenation of furan (**19**) in ROH) yields epoxylactone **54**, hydroxy butenolide (**78**), and the alkoxy butenolides **22**, **23** and **80**.

We encountered epoxylactone **54** as a rearrangement product of **20** in aprotic solvents (see above). It was formed together with diepoxide **53**. Polar solvents favored the production of **54**. Since diepoxide **53** is stable in ROH, it is not a precursor of the butenolides **78** and **22**, **23** and **80**. We therefore believe that **54** is formed via biradicals **20a** and **20b** as in aprotic solvents, and that the polarity of ROH favors the exclusive 1,2-H shift in **20b** to yield epoxylactone **54**.

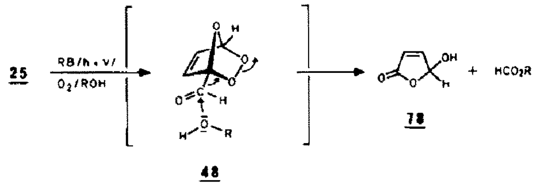
Under the reaction conditions applied by us, **78** and **22**, **23** and **80** are not interconvertible. We therefore suggest that there are two polar processes of **20** with ROH which compete with the homolytic cleavage of the O—O bond in **20**: first, the nucleophilic substitution to afford the alkoxy hydroperoxides **79** which eliminate water to yield the alkoxy butenolides **22**, **23** and **80**, and second, the rearrangement of **20** to hydroxy butenolide (**78**) induced by a base-catalyzed proton elimination from the bridgehead position of **20**, with ROH acting as the base (Scheme 2).



	54	78	
in MeOH	44%	21%	**22** R = CH_3, 35%
in EtOH	29%	58%	**23** R = CH_2-CH_3, 13%
in i-PrOH	28%	47%	**80** R = $CH(CH_3)_2$, 25%

Interestingly enough, if furfural (**25**) is photooxygenated in MeOH and EtOH, the only products obtained would be the hydroxy butenolide (**78**) and the corresponding ester of formic acid.[29]

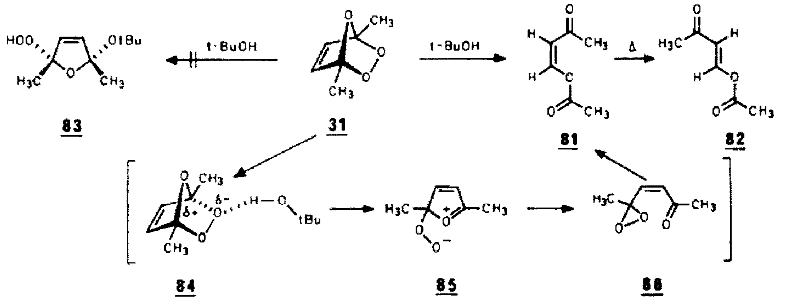
If the interaction of the expected ozonide intermediate **48** with ROH would occur similar to that of the Me derivative **46** with ROH, we should obtain formic acid and the butenolides **22** and **23**, respectively. Since formic acid and butenolides **22** and **23** are not converted to hydroxy butenolide (**78**) and the corresponding esters of formic acid under our reaction



conditions, the hydroxy butenolide (**78**) and methyl formate (or ethyl formate) are, in our opinion, the result of an attack of ROH on the CO group of **48**. Competing processes, such as observed with the other furans, have obviously no chance to occur.

Thus, depending on the structure of the ozonide, there are three pathways open for interaction of ROH with an ozonide: (a) addition of ROH to give alkoxy hydroperoxides; this pathway is taken only if the developing cation is stabilized by an alkyl group or by an alkoxy group; (b) elimination of a bridgehead proton by ROH as the base; (c) attack of ROH on a side-chain carbonyl substituent and elimination of the corresponding alkyl ester. Homolysis of the O—O bond of the ozonide may compete with these reactions.

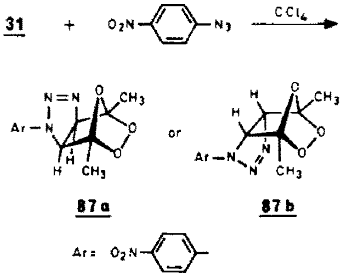
As we have seen above, ozonide **31** derived from 2,5-dimethylfuran (**30**) reacts with MeOH, EtOH and i-PrOH to give the *cis*-isomer **62–64**. If, however, **31** is reacted with t-BuOH, *cis*-3-oxo-1-butenylacetate (**81**) is quantitatively formed.



An attack of t-BuOH on **31** according to that of MeOH of Scheme 1 appears to be sterically hindered; t-butoxy hydroperoxide **83** could not be detected. Since interactions of t-BuOH with **31** corresponding to paths (b) and (c) as discussed above are impossible to occur, and since O—O bond homolysis of **31** is too slow, a Baeyer–Villiger-type rearrangement of **31** to **81** with vinyl group migration rather than Me group migration gets a chance to take place. This rearrangement should be induced by t-BuOH-assisted heterolysis of a C—O bond to give **84** (*cf.* with Scheme 1). The rearrangement may then proceed via the carbonyl-oxide **85** and the dioxirane **86** to give the *cis*-oxo-enolacetate **81** which may be thermally rearranged to the corresponding *trans*-**82**. Baeyer–Villiger-type rearrangement of an ozonide via a carbonyl-oxide and the corresponding dioxirane was recently discussed by Adam and Rodriguez.[30]

4. *Addition reactions to the C—C double bond of unsaturated ozonides*

An out-look on further studies. Since unsaturated ozonides such as **31** are now easily available, addition reactions to the C—C double bond should be studied. Adam *et al.*[31] have recently shown that treatment of **31** with diimine yields the corresponding saturated ozonide exclusively. If we added *p*-nitrophenyl azide to **31** dissolved at 0° in CCl_4, we obtained an addition product (m.p. 110–113°, dec) at a yield of 83%. According to elemental analysis, molecular weight determination (osmometric in acetone), ^1H- and ^{13}C-NMR spectra (the latter showing only one set of ^{13}C-signals) a [3+2]-cycloaddition product of structure **87a** or **87b** was formed in a completely stereoselective 1,3-dipolar cycloaddition reaction. Further reactions are presently carried out in our laboratory.



5. *Kinetic results*

Photooxygenation of furans in methanolic solution. Our method of determination of β-values defined as k_d/k_r (M), with k_d = 1/lifetime of $^1O_2$, and k_r = rate constant of $^1O_2$-reaction with a substrate, was recently published.[23,24a,25,26] β-values of furans, obtained from oxygen-uptake curves, are given in Table 2. With a singlet oxygen lifetime of 7×10^{-6} s in MeOH,[32] the rate constants k_r^{MeOH} are shown in Table 2. Clennan and Mehrsheikh-Mohammadi[33] have recently determined k_r in methylene chloride for a series of furans; their results are also shown in Table 2. It is interesting to note that the same trend of k_r is observed for the two solutions. Furthermore, the absolute values, although determined by different methods, appear to be very similar for the two solvents. This result is in accord with the fact that (4+2)-cycloaddition reactions of singlet

Table 2. Absolute rates of singlet oxygen reactions with furans in methanolic solution at 13°

Furan	$10^2\beta$(MeOH) (M)	$10^{-7}k_r^{MeOH}$ ($M^{-1}s^{-1}$)	$10^{-7}k_r^{CH_2Cl_2}$* ($M^{-1}s^{-1}$)
30	0.0781	18.3	13.0
42	0.0924	15.5	12.0
26	0.1400	9.9	6.2
19	1.607	0.89	1.2
41	8.412	0.17	—
25	169.80	0.0084	0.0051

* Ref. 33.

oxygen with *cis*-1,3-diene systems are insensitive towards the solvents[25,26] suggesting a concerted Diels–Alder reaction occurs.

With furans **30**, **42**, **26** and **19**, oxygen-uptake curves with time are linear and exactly the same if applied at concentrations distinctly larger than their half-value concentrations β (Table 2). Thus, these furans may be used to determine the limiting quantum yields of singlet oxygen formation or to determine the limiting rate of oxygen-consumption (see, e.g. refs 25, 26). 2,5-Dimethylfuran (**30**), however, is not only the fastest singlet oxygen acceptor of the furans studied here, but also gives rise to a rather stable ozonide the subsequent thermal reactions of which do not interfere with the singlet oxygen reaction of **30**. 2,5-Dimethylfuran, an inexpensive chemical, is therefore recommended as a standard acceptor for kinetic studies of singlet oxygen reactions.

EXPERIMENTAL

Chemicals. Compounds **19**, **26**, **30**, **39** and **42** (Ega) were used without further purification. Compounds **24**, **40**, **41** and **25** (Ega) were purified by distillation (**24**: 170–171°/730 Torr; **40**: 61–63°/12 Torr; **41**: 185–188°/730 Torr; **25**: 160–163°/730 Torr). Solvents (Fluka, puriss. p.a.) were used without further purification. Rose bengal (RB) (Ega), purified by extraction with MeOH, polymer-bound rose bengal (p-RB) (Hydron), purified by Soxhlet-extraction with acetone, and meso-tetraphenylporphin (TPP) prepared after ref. 34 and purified by chromatography on neutral alumina in hot CHCl$_3$,[35] were used as sensitizers.

Spectra. Proton-NMR spectra were recorded with CDCl$_3$ or mixtures of freon 11 (CFCl$_3$) and CDCl$_3$ as solvents on a Bruker WP-80-CW-spectrometer and on a Varian A-60-CW-spectrometer with TMS as internal standard. ^{13}C-NMR spectra were recorded on a Bruker WP-80-FT-spectrometer and on a Varian XL-100-FT-spectrometer using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer-IR-spectrometer 125 as thin films. M.ps are uncorrected.

Irradiation. For kinetic studies and small preparative runs, a 25 ml irradiation unit with automatic O$_2$-consumption recording system[36,37] was used. A 150 W Halogen-Bellaphot lamp (Osram) and a band filter, transparent between 480 and 570 nm (Hoya), was used for electronic excitation of RB and TPP. Both sensitizers were applied in concentrations of 2×10^{-4}, 4×10^{-4}, 6×10^{-4} and 10^{-3}M. The irradiation unit, the oxygen burette and the tubing connecting the unit with the burette were kept at (13±0.1)°, by cooling with water; thermostat JULABO-P.

For preparative photooxygenations at low temps, a soln of the substrate in freon 11 (CFCl$_3$) and CDCl$_3$ with TPP as sensitizer (10^{-3}M) in a 3-necked 50 ml flask with an O$_2$ inlet and a bubble gauge, cooled with a dry ice/acetone bath was irradiated with a 500 W Halogen-Argaphoto lamp (Philips). The soln was periodically sampled and the sample analyzed by ^{1}H-NMR spectroscopy at low temp. For preparative photooxygenations at 13°, a 150 ml irradiation unit with automatic O$_2$-consumption recording system was used.[16] A 150 W Hg-high-pressure lamp (Philips) and a cut-off filter (< 380 nm) was used. The irradiation unit, the oxygen burette and the tubing connecting the unit with the burette were kept at (13±0.1)° by cooling with water; thermostat LAUDA WB 20. CAUTION: Precautions should be taken according to the high instability of monomeric ozonides.

Products

1,4-Dimethyl-2,3,7-trioxa-bicyclo-[2.2.1]-hept-5-ene **31**. A soln of 500 mg **30** (5.2 mmol) in 25 ml CFCl$_3$ containing 500 mg p-RB was irradiated for 2.5 hr at 13°, after which time the O$_2$ consumption ceased and 5.2 mmol of O$_2$ was taken up. The solvent was removed at −15°/0.1 Torr and the residue was distilled at 5°/10^{-3} Torr into a trap cooled to −78°. The resulting yellowish oil (about 400 mg) violently exploded when warmed up to temps higher than −10°. In smaller amounts (< 100 mg), **31** could be stored some hours at room temp and CH-analysis and molecular weight could be obtained. ^{1}H-NMR: δ 1.70 (s, 6H); 6.25 (s, 2H). ^{13}C-NMR: δ 13.48 (q, 2CH$_3$); 112.34 (s); 124.12 (d). Mol. weight: 128 (calc), 144 (osmometric in benzene). (Found: C, 56.25; H, 6.30. C$_6$H$_8$O$_3$ requires: C, 56.25; H, 6.29%.)

1,4,7,10-Tetramethyl-2,3,8,9,13,14-hexaoxo-tricyclo-$[8.2.1.1^{4,7}]$*-tetradeca-5,11-diene* **38**. A soln of 1 g **30** (10.4 mmol) in a mixture of 80 ml benzene and 40 ml petrol ether containing 100 mg TPP was irradiated at 13° for 3 hr until the O$_2$ consumption ceased. After 24 hr at 20°, inspection of the ^{1}H-NMR spectrum showed that **31** was entirely converted into **38** in addition to some polymeric material. After removal of the solvents under reduced pressure, 10 ml ether and 10 ml petrol ether were added. After 2 hr, yellow crystals precipitated from the soln; 300 mg of **38** (23%) was isolated by filtration and sublimation at 120–130°/0.2 Torr. M.p. 143° (dec) (m.p. 154°[18]). ^{1}H-NMR: δ 1.82 (s, 12H); 6.34 (s, 4H). Mol. weight: 256 (calc), 254 (osmometric in benzene). (Found: C, 56.13; H, 6.42. C$_{12}$H$_{16}$O$_6$ requires: C, 56.25; H, 6.29%.)

General procedure for the preparation of monomeric ozonides at low temp. A soln of 340 mg **19** (5 mmol) and 5 mg TPP in a mixture of 10 ml CFCl$_3$ and 5 ml CDCl$_3$ was irradiated for 3 hr. During the irradiation, dry O$_2$ was bubbled through the soln which was kept at −78°. The soln was periodically analyzed by ^{1}H-NMR spectroscopy. After 2 hr the reaction was complete; the ozonide which precipitated from the soln was filtered off (glass frit at −60°). *2,3,7-Trioxa-bicyclo-*[2.2.1]*-hept-5-ene* **20**: colorless crystals which explode violently at temps above about −15°. ^{1}H-NMR: δ 6.24 (s, 2H); 6.38 (s, 2H). ^{13}C-NMR: δ 102.98 (d); 131.39 (d).

The monomeric ozonides **43**, **45**, **27**, **44**, **46** and **47** were prepared according to the procedure described above, from furans **24**, **40**, **26**, **39**, **41**, and **42**, respectively. The physical and spectral data of these ozonides are as follows:

1-Hydroxymethyl-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene* **43**. Yellowish crystals, exploding above about −30° to −20°. ^{1}H-NMR (−70°): δ 4.30 (m, 2H); 5.17 (m, 1H, OH); 6.62 (m, 3H).

1-Acetyl-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene* **45**. Yellow crystals, exploding at temps higher than −40°. ^{1}H-NMR (−70°): δ 2.54 (s, 3H, COCH$_3$); 6.73 (m, 1H); 6.83 (m, 2H).

1-Methyl-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene* **27**. Oil, decomposition point ~ 0°. ^{1}H-NMR (−50°): δ 1.79 (s, 3H); 6.15 (m, 2H); 6.31 (m, 1H). ^{13}C-NMR (−50°): δ 13.08 (q); 103.89 (d); 111.93 (s); 131.79 (d); 133.85 (d).

1-Ethyl-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene* **44**. Oil, decomposition point > −10°. ^{1}H-NMR (−60°): δ 1.17 (t, 3H); 2.20 (q, 2H); 6.30 (s, 1H); 6.40 (m, 2H). ^{13}C-NMR (−50°): δ 7.99 (q); 20.21 (t); 103.74 (d); 114.77 (s); 131.59 (d); 132.81 (d).

1-Methyl-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene-4-aldehyd* **46**. Yellowish oil, decomposition point > +10°. ^{1}H-NMR (−20°): δ 1.98 (s, 3H); 6.50 (d, 1H, J = 5.6 Hz); 6.77 (d, 1H, J = 5.6 Hz); 9.83 (s, 1H, CHO).

1-Methoxy-2,3,7-trioxa-bicyclo-[2.2.1]*-hept-5-ene* **47**. Obtained only in CFCl$_3$ soln. ^{1}H-NMR (−70°): δ 3.72 (s, 3H, OCH$_3$); 6.05 (m, 3H).

Reduction of ozonides **27**, **31**, **38** *and* **44** *with triphenylphosphane*

A soln of 2.05 g of triphenylphosphane (7.8 mmol) in 15 ml petrol ether was added slowly to a soln of 5.2 mmol **31** or **38** in 25 ml benzene cooled to 0°. After stirring the mixture for 1 hr, the ppt (triphenylphosphane oxide) was filtered off and the solvents removed at reduced pressure. Sublimation of the residue at 73–80°/10 Torr yielded 620 mg (93%) of yellowish needles of *trans-3-hexen-2,5-dione* **49** with m.p. 82–83° (m.p. 78°).[18] ^{1}H-NMR: δ 2.28 (s, 6H); 6.67 (s, 2H). (Found: C, 64.26; H, 7.32. C$_6$H$_8$O$_2$ requires: C, 64.27; H, 7.19%.) The diones **50** and **51** were prepared from **27** and **44**, respectively, as described for **49**.

trans-3-*Acetylacrolein* **50**. B.p. 72–74°/10 Torr (b.p. 72°/13 Torr).[18] ^{1}H-NMR: δ 2.35 (s, 3H); 6.69 (m, 2H); 9.68 (dd, 1H, CHO). (Found: C, 61.41; H, 6.08. $C_5H_6O_2$ requires: C, 61.22; H, 6.17%.)

trans-3-*Propionylacrolein* **51**. B.p. 88–91°/12 Torr. ^{1}H-NMR: δ 1.07 (t, 3H); 2.22 (q, 2H); 7.15 (m, 2H); 9.85 (dd, 1H, CHO). (Found: C, 64.22; H, 7.41. $C_6H_8O_2$ requires: C, 64.27; H, 7.19%.)

General procedure for the thermal conversion of ozonides

Thermal conversion was carried out on a soln (1%) of the ozonide in dry CCl_4 or in mixtures of $CDCl_3$ and freon 11. Only in the case of **30** was heating to 60° necessary to complete the thermal conversion. In the case of ozonides **20**, **27** and **44**, standing at room temp for some hours was sufficient for quantitative conversion of the ozonides.

2,5-Dimethyl-2,3:4,5-diepoxy-2,3,4,5-tetrahydrofuran **52**. After 10 min heating of a soln of 2 mmol **31** in 25 ml CCl_4 to 60°, the solvent was removed under reduced pressure and the residue distilled at 10°/10^{-5} Torr. The resulting colorless liquid slowly polymerizes and partly undergoes hydrolysis at room temp. ^{1}H-NMR: δ 1.58 (s, 6H); 3.42 (s, 2H). (Found: C, 56.31; H, 6.30. $C_6H_8O_3$ requires: C, 56.25; H, 6.29%.)

If a soln of the dimer **38** in CCl_4 (1%) was heated for 20 min to 60°, inspection of the ^{1}H-NMR spectrum showed only signals of **52** in addition to broadened signals due to polymeric material.

2,3:4,5-Diepoxy-2,3,4,5-tetrahydrofuran **53**. After stirring a soln of 2.5 mmol **20** in 25 ml CCl_4 for 30 min at room temp, the solvent was removed under reduced pressure. The solid residue, distilled at 70–80°/0.2 Torr, gave 85 mg (34%) **53** as slight-yellow needles, m.p. 110–114° (dec). ^{1}H-NMR: δ 3.75 (s, 2H); 5.50 (s, 2H). ^{13}C-NMR: δ 50.01 (d, 2C); 91.02 (d, 2C). IR: 3450 (s), 2920 (s), 1800 (vw), 1725 (vw), 1625 (w) cm^{-1}. MS: 100 (M^{+}), 83 (100%), 55 (80%), 29 (40%). (Found: C, 47.49; H, 4.08. $C_4H_4O_3$ requires: C, 48.01; H, 4.03%.)

3,4-Epoxy-butyrolactone **54**. A soln of 500 mg **20** (7 mmol) in 150 ml CH_2Cl_2 was stirred at room temp. After 30 min, inspection of the ^{1}H-NMR spectrum of the soln showed that **20** was entirely converted to **53** and **54** in a ratio of 62% to 38%. Removal of the solvent under reduced pressure and distillation of the residue at 50–55°/0.3 Torr, yielded 160 mg (22%) **54** as a colorless oil. ^{1}H-NMR: δ 2.80 (d, 2H); 3.87 (dt, 1H); 5.61 (d, 1H). ^{13}C-NMR: δ 33.14 (t); 51.13 (d); 79.05 (d); 173.47 (s). (Found: C, 48.23; H, 4.11. $C_4H_4O_3$ requires: C, 48.01; H, 4.03%.)

2-Methyl-2,3:4,5-diepoxy-2,3,4,5-tetrahydrofuran **58**. After 24 hr stirring of a soln of 170 mg **27** in 25 ml CCl_4 at room temp, inspection of the ^{1}H-NMR spectrum showed that **27** was entirely converted into **58** and **59** in a ratio of 90% to 10%. After removal of the solvent under reduced pressure, the residue was distilled at 10–15°/10^{-5} Torr. The resulting colorless oil was a mixture of 90% **58** and 10% *4-methyl-3,4-epoxy-butyrolactone* **59** (according to the ^{1}H-NMR spectrum). All attempts to isolate the pure compounds by distillation or chromatographic methods failed since **58** and **59** rapidly polymerized at room temp. ^{1}H-NMR (**58**): δ 1.62 (s, 3H); 3.42 (m, 1H); 3.52 (m, 1H); 5.25 (d, 1H). ^{13}C-NMR (**58**): δ 16.66 (q); 51.12 (d); 54.91 (d); 88.56 (d); 99.23 (s). ^{1}H-NMR (**59**): δ 1.55 (s, 3H); 2.85 (s, 2H); 3.77 (s, 1H). ^{13}C-NMR (**59**); δ 15.33 (q); 34.71 (t); 56.18 (d); 87.63 (s); 173.83 (s).

2-Ethyl-2,3:4,5-diepoxy-2,3,4,5-tetrahydrofuran **60**. A soln of 350 mg of **44** in 25 ml CH_2Cl_2 was stirred for 24 hr at 20°. Removal of the solvent under reduced pressure and distillation of the residue at 0°/10^{-5} Torr yielded a mixture of 61% **60** and 39% *4-ethyl-3,4-epoxybutyrolactone* **61**. All attempts to isolate the pure compounds by distillation or chromatographic methods failed; **60** and **61** rapidly polymerized at room temp. ^{1}H-NMR (**60**): δ 1.03 (t, 3H); 1.97 (q, 2H); 3.69 (m, 2H); 5.40 (d, 1H). ^{13}C-NMR (**60**): δ 8.62 (q); 23.35 (t); 51.04 (d); 54.02 (d); 88.52 (d); 102.33 (s). ^{1}H-NMR (**61**): δ 1.10 (t, 3H); 2.01 (q, 2H); 2.83 (s, 2H); 3.64 (s, 1H). ^{13}C-NMR (**61**): δ 8.01 (q); 21.77 (t); 34.41 (t); 54.89 (d); 91.22 (s); 173.69 (s).

General procedure for the preparation of alkoxy hydroperoxides

(a) A soln of 1 mmol of **27**, **31**, **44**, **47** or the dimeric ozonide **38** in 15 ml $CDCl_3$ was dissolved in 50 ml of dry alcohol pre-cooled to 0°. Warming up to 20° and stirring for 30 min, followed by removal of the solvent under reduced pressure (30–40°/10 Torr), afforded alkoxy hydroperoxides in quantitative yields. Solid products were twice recrystallized from petrol ether and liquid alkoxy hydroperoxides were dried over silica gel for 24 hr.

(b) A soln of 10 mmol of **26**, **30**, **39** or **42** in 150 ml of dry alcohol in the presence of 1 g p-RB was irradiated at 13° until the O_2-consumption ceased. After removal of the solvent under reduced pressure (30–40°/10 Torr), solid products were twice recrystallized from petrol ether and liquid products were dried over silica gel for 24 hr. Physical, spectral and analytical data of **62**–**67** and **71**–**76** are shown in Table 3.

4-Methoxy-4-methyl-butenolide **68**. A soln of 443 mg (3 mmol) **65** in 25 ml MeOH was added to a suspension of 900 mg (4.9 mmol) of vanadium pentoxide in 30 ml MeOH cooled to 0°. After stirring the mixture for 2 hr at room temp, the ppt was filtered off, and the solvent was removed at reduced pressure. Distillation of the residue at 25–33°/0.3 Torr yielded 275 mg (72%) of a colorless oil. ^{1}H-NMR: δ 1.65 (s, 3H); 3.22 (s, 3H); 6.20 (d, 1H, J = 6 Hz); 7.26 (d, J = 6 Hz). ^{13}C-NMR: δ 23.47 (q); 51.26 (q); 109.65 (s); 124.03 (d); 155.08 (d); 170.44 (s). (Found: C, 56.01; H, 6.13. $C_6H_8O_3$ requires: C, 56.25; H, 6.29%.)

The butenolides **69** and **70** were prepared, as described for **68**, from **66** and **67** with yields of 51% and 42%, respectively. Spectral and physical data for **69** and **70** are as follows:

4-Ethoxy-4-methyl-butenolide **69**. Oil; b.p. 88–91°/12 Torr. ^{1}H-NMR: δ 1.18 (t, 3H, J = 7 Hz); 1.65 (s, 3H); 3.42 (2 dq, 2H); 6.13 (d, 1H, J = 5.3 Hz); 7.19 (d, 1H, J = 5.3 Hz).

4-iso-Propyloxy-4-methyl-butenolide **70**. Oil; b.p. 50–53°/0.3 Torr. ^{1}H-NMR: 1.12 (d, 3H, J = 6 Hz); 1.17 (d, 3H, J = 6 Hz); 1.63 (s, 3H); 3.71 (sept., 1H); 6.17 (d, 1H, J = 6.5 Hz); 7.12 (d, 1H, J = 6.5 Hz).

2-Formyl-2-hydroperoxy-5-methyl-5-methoxy-2,5-dihydrofuran **77**

A soln of 100 mg of **41** (0.91 mmol) and 30 mg of RB in 20 ml MeOH was irradiated for 4 hr at −78°. Then the soln was warmed up to −15° and stirred for 2 hr. After removal of the solvent at −15°/10^{-4} Torr the residue was dissolved in $CDCl_3$ and the ^{1}H-NMR spectrum was recorded at −52°. ^{1}H-NMR (−52°): δ 1.92 (s, 3H); 3.46 (s, 3H); 6.38 (d, 1H, J = 4 Hz); 7.41 (d, 1H, J = 4 Hz); 9.44 (s, 1H, CHO).

When the soln of **77** in $CDCl_3$ was stirred for 1 hr at room temp, **77** had quantitatively eliminated formic acid and formed **68**. Formic acid was distilled at 40–50°/10 Torr after the alcohol was removed at reduced pressure.

Similar observations were made with the photooxygenation reactions of **41** in EtOH or i-PrOH at 13°, where **69** and **70** were formed quantitatively.

4-Hydroxybutenolide **78**. A soln of 2 g **25** (20.8 mmol) in 150 ml MeOH (2 × 10^{-4}M soln of RB) was irradiated for 8 hr at 13°. After removal of the solvent at reduced pressure, the solid yellow residue was recrystallized from MeOH, yielding 1.1 g of **78** (53%). M.p. 49–53° (m.p. 55°).[12] ^{1}H-NMR: δ 5.68 (s, OH); 6.19 (d, 1H, J = 5.1 Hz); 6.24 (s, 1H); 7.36 (d, 1H, J = 5.1 Hz). ^{13}C-NMR: δ 99.53 (d); 124.12 (d); 153.05 (d); 172.34 (s). (Found: C, 47.78; H, 4.05. $C_4H_4O_3$ requires: C, 48.01; H, 4.03%.)

4-Methoxy-butenolide **22**. A soln of 1 mmol **20** in 25 ml $CHCl_3$ cooled to −20° was dissolved in 10 ml of dry MeOH pre-cooled to −20°. Warming to 20° and stirring for 1 hr, followed by removal of the solvents and methyl formate (30–32°/730 Torr), afforded a mixture of 44% **54**, 21% **78** and 35% **22** (according to the ^{1}H-NMR spectrum). Distillation at 45–48°/0.1 Torr yielded **22** as a colorless oil (22%). ^{1}H-NMR: δ 3.41 (s, 3H); 5.73 (dd, 1H, J_1 = 1 Hz, J_2 = 1.2 Hz); 6.13 (dd, 1H,

Table 3. M.ps, ^1H- and ^{13}C-NMR data, and elemental analysis of alkoxy hydroperoxides (**62–67** and **71–76**)

Product	M.p. (°)	^1H ($CDCl_3$)(J/Hz)	^{13}C ($CDCl_3$/ppm	Formula	Analysis (%) Found (required) C	H
62	79–80	1.47 (s, 3H, CH_3) 1.53 (s, 3H, CH_3) 3.33 (s, 3H, OCH_3) 5.99 (AB-system, 2H) 8.63 (s, 1H, OOH)	22.26 (q) 25.11 (q) 51.01 (q) 111.55 (s) 114.16 (s) 131.64 (d) 134.64 (d)	$C_7H_{12}O_4$	52.62 (52.49)	7.65 (7.55)
63	oil	1.17 (t, 3H, J/7) 1.49 (s, 3H, CH_3) 1.55 (s, 3H, CH_3) 3.62 (m, 2H, O—CH_2—) 5.95 (AB-system, 2H) 8.88 (s, 1H, OOH)	15.51 (q) 22.35 (q) 25.59 (q) 58.85 (t) 111.22 (s) 114.07 (s) 131.33 (d) 135.09 (d)	$C_8H_{14}O_4$	55.25 (55.16)	8.13 (8.06)
64	oil	1.13 (d, 3H, J/6) 1.18 (d, 3H, J/7) 1.50 (s, 6H) 4.11 (qq, 1H, J/6/7) 5.93 (AB-system, 2H) 8.87 (s, 1H, OOH)	22.35 (q) 24.17 (q) 24.32 (q) 25.84 (q) 64.64 (d) 111.16 (s) 114.09 (s) 130.99 (d) 135.54 (d)	$C_9H_{16}O_4$	57.21 (57.43)	8.69 (8.57)
65	80–82	1.54 (s, 3H) 3.23 (s, 3H, OCH_3) 6.03 (m, 3H) 8.72 (s, 1H, OOH)	25.81 (q) 50.92 (q) 109.53 (d) 112.52 (s) 126.58 (d) 136.97 (d)	$C_6H_{10}O_4$	49.37 (49.31)	6.73 (6.89)
66	74–76	1.16 (t, 3H) 1.54 (s, 3H), 3.48 (m, 2H, O—CH_2—) 6.02 (m, 3H) 8.67 (s, 1H, OOH)	15.38 (q) 26.08 (q) 58.85 (t) 109.47 (d) 112.21 (s) 125.93 (d) 137.73 (d)	$C_7H_{12}O_4$	52.64 (52.49)	7.53 (7.55)
67	oil	1.02 (d, 3H, J/9.4) 1.12 (d, 3H, J/10) 1.57 (s, 3H) 4.02 (qq, 1H, J/9.4/10) 6.06 (m, 3H) 8.65 (s, 1H, OOH)	23.93 (q) 24.26 (q) 26.59 (q) 65.33 (d) 109.37 (d) 112.13 (s) 125.73 (d) 137.97 (d)	$C_8H_{14}O_4$	55.18 (55.16)	7.93 (8.10)
71	96–98	0.85 (t, 3H, J/7) 1.83 (q, 2H, J/7) 3.23 (s, 3H) 5.98 (m, 3H) 10.11 (s, 1H, OOH)	7.99 (q) 31.59 (t) 50.75 (q) 109.56 (d) 115.46 (s) 127.46 (d) 135.60 (d)	$C_7H_{12}O_4$	52.62 (52.49)	7.29 (7.55)
72	107–110	0.86 (t, 3H, J/7) 1.17 (t, 3H, J/7.2) 1.87 (q, 2H, J/7) 3.49 (2 dq, 2H) 5.97 (s, 1H) 6.00 (m, 2H) 9.78 (s, 1H, OOH)	8.06 (q) 15.39 (q) 31.84 (t) 58.70 (t) 109.53 (d) 115.19 (s) 126.79 (d) 136.33 (d)	$C_8H_{14}O_4$	55.27 (55.16)	7.99 (8.10)
73	oil	0.84 (t, 3H, J/7.4) 1.04 (d, 3H, J/9) 1.12 (d, 3H, J/10) 1.71 (q, 2H, J/7.4) 3.89 (qq, 1H, J/10/9) 5.89 (m, 3H) 8.99 (s, 1H, OOH)	8.14 (q) 24.02 (q) 24.61 (q) 32.09 (t) 65.41 (d) 109.24 (d) 112.61 (s) 126.06 (d) 137.12 (d)	$C_9H_{16}O_4$	57.47 (57.43)	8.79 (8.57)
74	oil	3.59 (s, 3H) 3.75 (s, 3H) 5.94 (d, 1H, J/11) 6.12 (s, 1H) 6.17 (dd, 1H, J/11/5.8) 8.69 (s, 1H, OOH)	51.79 (q) 56.34 (q) 102.44 (d) 122.73 (d) 140.63 (d) 165.86 (s)	$C_6H_{10}O_5$	44.78 (44.45)	6.14 (6.22)
75	oil	1.25 (t, 3H, J/7.2) 3.73 (s, 3H) 3.80 (2dq, 2H) 5.94 (m, 1H) 6.23 (m, 2H) 8.94 (s, 1H, OOH)	15.21 (q) 51.70 (q) 64.94 (t) 101.35 (d) 122.39 (d) 141.06 (d) 165.80 (s)	$C_7H_{12}O_5$	47.60 (47.73)	7.09 (6.86)
76	oil	1.19 (d, 3H, J/11) 1.31 (d, 3H, J/12) 3.73 (s, 3H, OCH_3) 4.13 (qq, 1H) 5.80–6.45 (m, 3H) 9.14 (s), 1H, OOH)	22.17 (q) 23.23 (q) 51.67 (q) 71.51 (d) 99.62 (d) 121.76 (d) 141.54 (d) 165.86 (s)	$C_8H_{14}O_5$	50.17 (50.52)	7.63 (7.42)

$J_3 = 5.2$ Hz, $J_2 = 1.2$ Hz); 7.09 (dd, 1H, $J_3 = 5.2$ Hz, $J_1 = 1$ Hz). (Found: C, 52.73; H, 5.21. $C_5H_6O_2$ requires: C, 52.63; H, 5.26%.)

Butenolides **23** and **80** were prepared as described for **22** with yields of 15% and 18%, respectively.

4-*Ethoxy-butenolide* **23**. ^1H-NMR: δ 1.23 (t, 3H, J = 7 Hz); 3.63 (m, 2H); 5.65 (s, 1H); 6.03 (d, 1H, J = 4 Hz); 7.22 (d, 1H, J = 4 Hz).

4-*iso-Propyloxy-butenolide* **80**. ^1H-NMR: δ 1.21 (d, 6H, J = 6.5 Hz); 3.99 (m, 1H); 5.64 (s, 1H); 6.16 (d, 1H, J = 5.6 Hz); 7.28 (d, 1H, J = 5.6 Hz).

cis-3-*Oxo*-1-*butenylacetate* **81**. A soln of 500 mg **30** (5.2 mmol) in a mixture of 18 ml t-BuOH and 7 ml $CHCl_3$ was irradiated in the presence of 500 mg p-RB until the O_2 consumption ceased (1.3 hr). Filtration of the sensitizer and removal of the solvent under reduced pressure (25°/10 Torr), followed by distillation at 67–70°/10 Torr yielded 440 mg of **81** (67%) as a yellow oil. ^1H-NMR: δ 2.29 (s, 3H); 2.41 (s, 3H); 5.45 (d, 1H, J = 7 Hz); 7.60 (d, 1H, J = 7 Hz). IR: 1760, 1670, 1355, 1175, 1060, 1005, 800, 687 cm^{-1}. (Found: C, 56.12; H, 6.24. $C_6H_8O_3$ requires: C, 56.25; H, 6.29%.)

Prolonged heating of **81** at temps above about 120° converted **81** quantitatively into the *trans*-isomer **82**: trans-3-*Oxo*-1-*butenylacetate*. b.p. 74–76°/10 Torr. ^1H-NMR: δ 2.25 (s, 3H); 2.31 (s, 3H); 5.85 (d, 1H, J = 13 Hz); 8.10 (d, 1H, J = 13 Hz). (Found: C, 55.82; H, 6.34. $C_6H_8O_3$ requires: C, 56.25; H, 6.29%.)

2,5-*Dimethyl*-7-(4-*nitro*-*phenyl*)-7,8,9-*triaza*-3,4,10-*trioxa-tricyclo*-[4.3.1^{2,5}0]-*deca-8-ene* **87**

A soln of 269 mg **31** (2.1 mmol) in 25 ml CCl_4 was added to a soln of 345 mg *p*-nitrophenyl azide (2.1 mmol) in 30 ml CCl_4 pre-cooled to 0°. After 24 hr stirring at room temp, the ppt was filtered off and dried: 510 mg (83%); m.p. 110–113° (dec). MS: 232 ($M^+ - N_2 - O_2$, 1%). ^1H-NMR: δ 1.60 (s, 3H); 1.90 (s, 3H); 4.29 (d, 1H, J = 8.2 Hz); 5.31 (d, 1H, 8.2 Hz); 7.29 (d, 2H, 9.6

Hz); 8.28 (d, 2H, 9.6 Hz). ^{13}C-NMR: δ 12.36 (q); 13.17 (q); 60.12(d); 89.32(d); 110.13(s); 111.07(s); 114.58(d); 125.85(d); 142.99 (s); 145.11 (s). Molecular weight: 292 (calc), 281 (osmometric in acetone). (Found: C, 49.19; H, 4.09; N, 19.25. $C_{12}H_{12}N_4O_5$ requires: C, 49.32; H, 4.14; N, 19.17%.)

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