

THE 185 nm PHOTOLYSIS OF SUBSTITUTED 1,3-DIOXOLANS IN THE LIQUID PHASE: STEREOSELECTIVITY ALONG SOME OF THE REACTION PATHWAYS

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Summary

The UV photolysis of *cis*- and *trans*-2,2,4,5-tetramethyl-1,3-dioxolans in the liquid phase gives, among other products, *cis*- and *trans*-2-butene and *cis*- and *trans*-2,3-dimethyl-oxiran which show substantial retention of the diastereoisomeric disposition. The photolysis of three diastereoisomeric 4,5-cyclohexano-2-methyl-1,3-dioxolans reveals that in 1,3-dioxolans, as in acyclic acetals, both types of C—O bond are cleaved.

1. Introduction

Saturated ethers and acetals start to absorb at around 200 nm. Their first absorption band is attributed to an $n \rightarrow \text{Rydberg}$ transition. The photochemistry at 185 nm in the liquid phase of several compounds of these types has been studied in some detail [1, 2]. It has been shown that the most important process is the scission of a C—O bond leading to alkoxy and alkyl radicals or to alkyl oxyl biradicals if the educt is a cyclic compound. Alkoxy radicals are known to undergo β fragmentation, particularly if they are branched (e.g. $(\text{CH}_3)_3\text{CO}^\cdot \rightarrow (\text{CH}_3)_2\text{C}=\text{O} + \cdot\text{CH}_3$; $k(25^\circ\text{C})$ is $3 \times 10^2 \text{ s}^{-1}$ in halocarbons [3] and is more than 10^6 s^{-1} in aqueous solution [4]), but they also readily abstract carbon-bound hydrogen atoms (e.g. $\text{CH}_3\text{O}^\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH} + \cdot\text{CH}_2\text{OH}$; $k(25^\circ\text{C})$ is $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [5]). In neat ethers the hydrogen donor concentration is so high that the latter process predominates and the fragmentation reactions of these radicals are suppressed. In agreement with this expectation the *n*-propoxyl radical which is the major alkoxy radical in the photolysis of liquid methyl-*n*-propyl ether [6] does not fragment at all but is stabilized by hydrogen abstraction.

The fate of alkyl oxyl biradicals formed in the photolysis of cyclic ethers is different from that of the free alkoxy and alkyl radicals generated from open-chain ethers. Both radical sites interact with each other either by reclosure or by disproportionation [7 - 9]. Intramolecular hydrogen

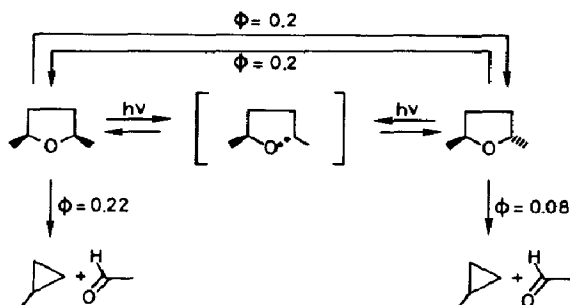
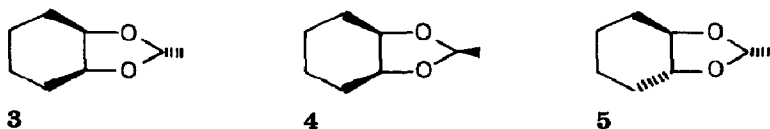


Fig. 1. *cis* \rightleftharpoons *trans* isomerization and methylcyclopropane formation in the UV photolysis of *cis*- and *trans*-2,5-dimethyltetrahydrofuran.

abstraction by the oxyl end has also been observed [9]. Biradical formation, however, is not the only reaction pathway in the photolysis of cyclic ethers. In the photolysis of tetrahydrofuran and its methyl derivatives [7] high yields of fragmentation products, cyclopropanes and the corresponding carbonyl compounds are formed (Fig. 1). (It should be noted that the quantum yields differ from the *cis* to the *trans* educt; this argues against the involvement of an alkyl oxyl 1,5 biradical.) A similar observation has been made with 1,4-dioxan which largely decomposes into formaldehyde and ethylene [10].

Olefin formation is observed in the 1,3-dioxolan series [11]. It is not clear whether this occurs by a true molecular process or via an alkyl oxyl biradical. The use of *trans*- and *cis*-2,2,4,5-tetramethyl-1,3-dioxolans (1 and 2) as substrates should allow a distinction to be made between these two processes. In a true molecular process the *cis* or *trans* arrangement might be preserved in the olefin product, whereas with a biradical intermediate considerable equilibration or preferential formation of the more stable *trans* compound would be expected.

In the acyclic acetal series both types of C—O bonds are photolytically cleaved [12 - 14]. In the photolysis of the 1,3-dioxolans studied previously [11] the observed products did not indicate the occurrence of C(2)—O(1) cleavage leading to the corresponding biradical, whereas a number of products were identified whose precursor must be assumed to be the biradical originating from O(1)—C(5) cleavage. C(2)—O(1) cleavage followed by reclosure, however, was then an undetectable reaction because it merely led back to the educt. If suitably substituted 1,3-dioxolans are chosen it should be possible to monitor such a biradical if it lasts long enough and inverts at the radical centre to form the diastereoisomer. The compounds 3 - 5 constitute such a set:



It will be shown that both types of cleavage do in fact occur.

2. Experimental details

Both *cis*- and *trans*-2,2,4,5-tetramethyl-1,3-dioxolans (1 and 2) were synthesized from a commercially available mixture of the 2,3-butanediols (about 90% racemic and 10% *meso*) and acetone [15]; the three 4,5-cyclohexano-2-methyl-1,3-dioxolans 3, 4 and 5 were prepared from a commercially available mixture of *cis*- and *trans*-cyclohexane-1,2-diols and paraldehyde. The products were resolved by preparative gas chromatography (GC). The configuration of the isomers was assigned on the basis of their proton magnetic resonance (PMR) spectra. Since the PMR spectra of the two *cis*-4,5-cyclohexano-2-methyl-1,3-dioxolans are very similar, it was in addition assumed that the major *cis* component (64% of total *cis*) was the 4,5-*cis*-2-*exo* isomer 3 and that the other component was the 4,5-*cis*-2-*endo* isomer 4. (The PMR spectral features for 3 were as follows: doublet, 1.44 ppm (3 H); broad absorption, 1.2 - 2.0 ppm (8 H); multiplets 4.02 ppm (2 H); quartet, 5.12 ppm (1 H). For 4 the spectrum was as follows: doublet, 1.33 ppm (3 H); broad absorption, 1.1 - 2.0 ppm (8 H); multiplet, 4.09 ppm (2 H); quartet, 5.42 ppm (1 H). For *trans*-4,5-cyclohexano-2-methyl-1,3-dioxolan (5) the spectrum was as follows: doublet, 1.39 ppm (3 H); broad absorption, 1.1 - 2.4 ppm (8 H); multiplet, 3.21 ppm (2 H); quartet, 5.30 ppm (1 H).) The isomers showed a gas chromatographic purity of better than 99.97% by flame ionization detection. The residual moisture in the 2,2,4,5-tetramethyl-1,3-dioxolans as determined by GC and thermal conductivity detection did not exceed 0.1%.

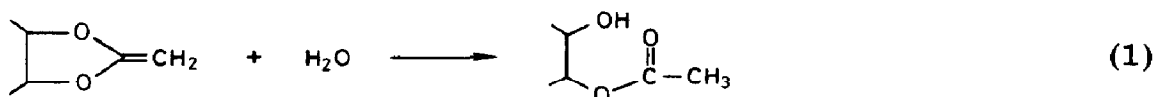
Samples (2 ml) of neat 2,2,4,5-tetramethyl-1,3-dioxolan contained in a Suprasil cell were deaerated by purging with argon for 30 min and irradiated with the unfiltered light of a low pressure mercury lamp at a dose rate determined using the Farkas actinometer [1] of 4.0×10^{17} quanta (185 nm) min^{-1} received by the sample. The 254 nm light is inactive in these systems. A photograph of the experimental arrangement is given and its use is described in ref. 16. The *trans* compound, similarly to the dioxolans studied previously [11], begins to absorb near 200 nm. $\epsilon(\lambda)$ ($\text{M}^{-1} \text{cm}^{-1}$) has the following values: 0.4 (197 nm); 0.65 (196 nm); 1.3 (195 nm); 2.7 (194 nm); 5.8 (193 nm); 11 (192 nm); 21 (191 nm). Conversions did not exceed 0.5%. The products were analysed by GC and identified using reference material and/or their mass spectra obtained by combined gas chromatography and mass spectrometry (GC-MS). Glass capillary columns coated with Marlophen (100 m long; operated in the temperature-programmed mode between 10 and 220 °C) and PPG 2000 (100 m long; isothermal at 0 °C) were suitable. Hydrogen was used as the carrier gas. The products were determined either by calibration or with the help of an internal standard (a saturated alkane). Evaluation was carried out using the method of the functional group GC response increments [17].

Samples of 0.063 M solutions of 3, 4 and 5 in cyclohexane were treated and irradiated as described above. Conversions reached 15%. The stereoisomeric products were measured isothermally at 80 °C on a Carbowax 20 M column 70 m long (carrier gas, hydrogen).

3. Results

The products of the photolysis of deaerated 2,2,4,5-tetramethyl-1,3-dioxolans and their quantum yields are given in Table 1. The values are assumed to be accurate to within 15%. The study of *cis*-tetramethyldioxolan was less detailed than that of *trans*-tetramethyldioxolan because there was less of it available. The stereospecificity in the formation of the butenes and the dimethyloxirans is of particular interest in this study. Attention is also drawn to educt isomerization.

The products are found to be largely as expected on the basis of previous work [11]. The product 2-(3-hydroxy)butyl acetate (see Table 1) deserves brief comment. It is probably formed by the reaction of the ketene acetal with residual moisture:



It is known that such ketene acetals have a very high affinity for water [19]. The formation of the hydroxyacetate can be completely suppressed if the tetramethyldioxolan is photolysed together with 20% methanol. In this case another product appears whose mass spectrum is identical with that of 2,4,5-trimethyl-2-methoxy-1,3-dioxolan (the reference material was synthesized from 2,3-butanediol and trimethylorthoacetate). This product is apparently formed by the reaction of the ketene acetal with the alcohol:



A similar ketene acetal is formed in the photolysis of acetaldehyde dimethyl acetal [13], whereas this reaction has not been detected in the photolysis of 2,2-dimethyl-1,3-dioxolan [11].

In the cyclohexanodioxolan series attention was paid only to the formation of stereoisomers. Their quantum yields are given in Table 2.

4. Discussion

4.1. Olefin and oxiran formation

The products of the photolysis of the *cis*- and *trans*-3,4-dimethyldioxolans listed in Table 1 can be explained within the general mechanistic framework of the 1,3-dioxolan photolysis developed earlier [11] but the present results enable more insight to be gained into the mechanisms of olefin and oxiran formation. Reaction (3) (Fig. 2) occurs with a high stereoselectivity. The *cis* compound gives largely *cis*-2-butene (about 97% of the

TABLE 1

The products and quantum yields of the 185 nm photolysis of liquid deaerated 2,2,4,5-tetramethyl-1,3-dioxolans (TMD)

<i>Products</i>	<i>trans-TMD</i>	<i>cis-TMD</i>
Hydrogen	< 0.001	NM
Carbon monoxide	0.003	0.008
Carbon dioxide	0.05	0.06
Methane	0.27	0.24
Ethylene	< 0.001	NM
Ethane	0.05	0.05
Acetone	0.08	NM
Isopropanol	< 0.01	NM
Methyl acetate	≈ 0.02	NM
<i>Cis</i> -2-butene	0.005	0.07
<i>Trans</i> -2-butene	0.065	0.002
Butanone	0.02	NM
<i>Cis</i> -2,3-dimethyloxiran	0.01	0.04
<i>Trans</i> -2,3-dimethyloxiran	0.03	0.01
2-(3-hydroxy)butyl acetate ^a	0.12	NM
2-but-3-enyl acetate ^b	0.03	NM
2-butyl acetate ^b	0.02	NM
5-methylene-2,2,4-trimethyl-1,3-dioxolan ^c	0.05	NM
2,2,4,4,5-pentamethyl-1,3-dioxolan ^d	≈ 0.01	NM
2-(3-methyl)butyl acetate ^b	0.14	NM
<i>Cis</i> -TMD	0.03	
<i>Trans</i> -TMD		0.07

NM, not measured.

^aThe reference material was synthesized from 2,3-butanediol and acetic anhydride using sodium acetate as catalyst.

^bThe reference material was synthesized from the alcohol and acetic acid; the water was entrained by methylene chloride and removed in a water take-off.

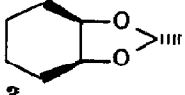
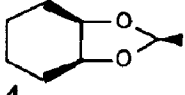
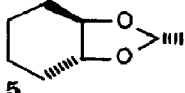
^cThe mass spectrum of the product indicates a molecular weight of 128. Prominent *m/e* peaks occur as follows: 43 (100%), 42 (82%), 59 (70%), 41 (40%), 70 (40%), 128 (30%), 71 (20%), 113 (15%) and 85 (7%). A reference material was not available. However, the mass spectrum of the easily accessible [18] homologue 2,2-dimethyl-4-methylene-1,3-dioxolan shows significant analogies (*m/e*: 43 (100%), 42 (60%), 71 (35%), 41 (30%), 72 (30%), 56 (25%), 114 (20%) and 99 (15%)) to that of the unknown, so that we can conclude that the product in question is the compound shown.

^dThe mass spectrum of the product indicates a molecular weight of 144. Prominent *m/e* peaks occur as follows: 43 (100%), 58 (50%), 87 (45%), 129 (30%), 59 (30%), 41 (22%), 69 (20%), 86 (20%), 42 (20%), 45 (15%) and 71 (10%).

total butene) and the *trans* compound gives largely *trans*-2-butene (about 93%). Therefore 2-butene cannot form through its triplet state because the triplet of the 2-butenes gives rise to both *cis*- and *trans*-butenes in about equal amounts [20, 21]. Nor can the five-membered alkyl oxyl biradical which is formed in reaction (5) and through which the *cis* → *trans* and

TABLE 2

UV photolysis of cyclohexanodioxolans: quantum yields of diastereoisomerization

Educt	$\phi(3)$	$\phi(4)$	$\phi(5)$
 3	—	0.02 ₁	0.02 ₁
 4	0.01 ₆	—	0.01 ₆
 5	0.01 ₅	0.01 ₀	—

trans → *cis* isomerization of the educts is believed to proceed by the precursor of the 2-butenes since this intermediate would also yield equilibrated 2-butenes. Moreover, it can be estimated that cleavage of the 1,5 biradical into butene and dioxiran (CH₃)₂CO₂ must be extremely endothermic. The assumption of dioxiran formation in 1,3-dioxolan photolysis is reasonable as it explains the formation of CO₂. Evidence for reactions such as (3-1) has been obtained in other contexts [22, 23].

It has been reported [24] that 2-butenes are formed from 2,4,5-trimethyl-1,3-dioxolan-2-yl radicals produced in the γ radiolysis of aqueous solutions of 2,4,5-trimethyl-1,3-dioxolans. Stereospecificity is much less pronounced in this case: 85% *trans* is obtained from the *trans* educt and 58% *cis* is obtained from the *cis* educt. Moreover, the formation of 2-butene in this case may involve an intermediate carbanion derived from the dioxolan-2-yl radical through charge dismutation. Similar species generated by deprotonation from the appropriate 1,3-dioxolans have been shown to yield olefins [25, 26]. Charge dismutation has been postulated for other radical systems [27].

The foregoing indicates that the dioxolan-2-yl radical cannot be a precursor of the butenes in the present system. In any case evidence from the photolysis of other acetals [12, 13] leads to the conclusion that the formation of the dioxolan-2-yl radical should not be a major process in this system. In summary it appears that the 2-butene is predominantly formed as a ground state molecule (reaction (3)).

Some retention of configuration is also observed in the formation of the epoxybutanes (reactions (4) and (4-1); 80% *cis* of the dimethyloxiran total from the *cis* educt versus 75% *trans* from the *trans* educt). This is taken as an indication that the oxiran precursor is not a triplet 1,3 biradical because then we would expect this biradical to have sufficient time available for randomization so that the same ratio of *cis* to *trans* dimethyloxirans

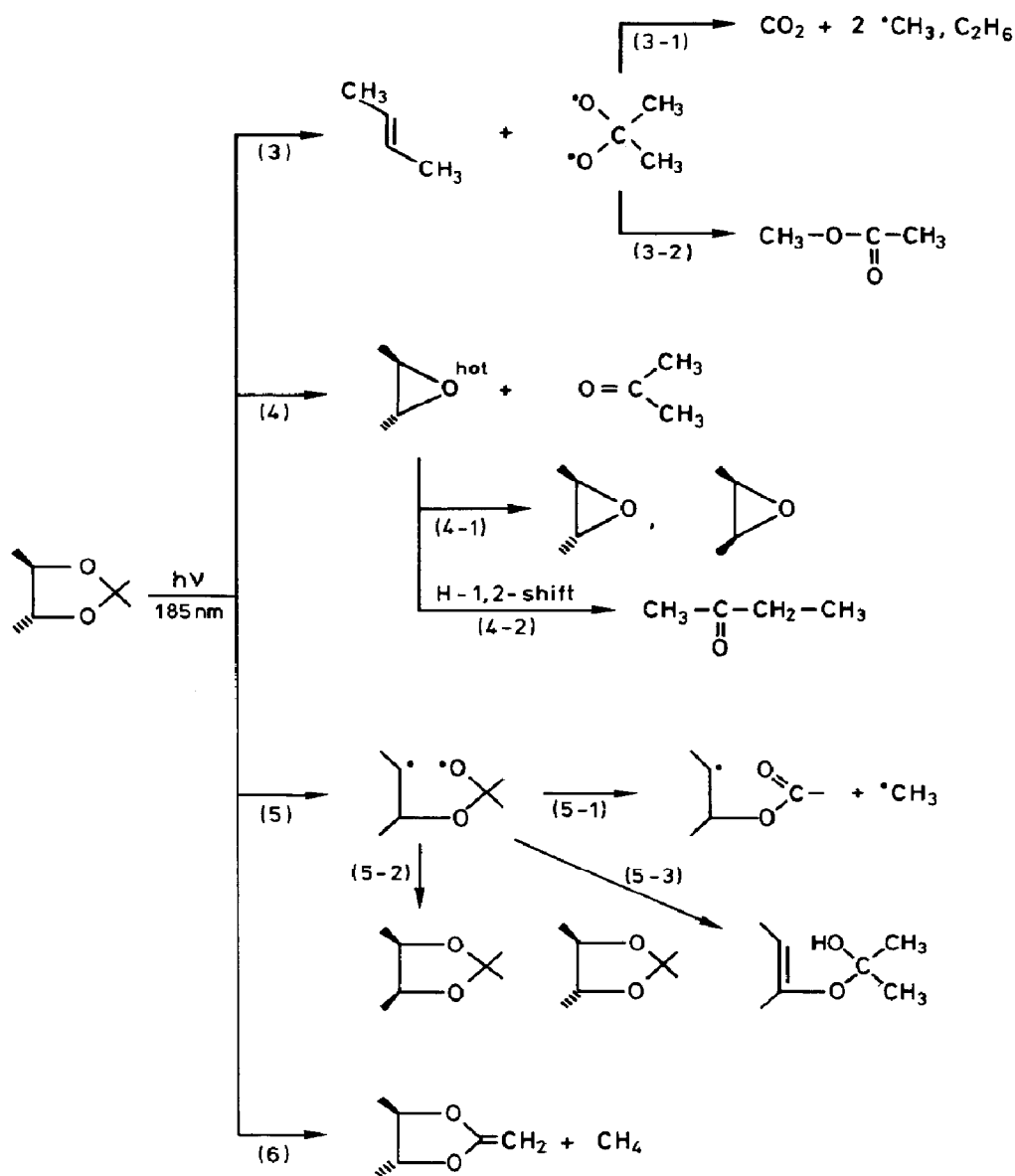


Fig. 2. Primary processes and some consecutive reactions in the 185 nm photolysis of *trans*-2,2,4,5-tetramethyl-1,3-dioxolan.

should be reached from both educts. In agreement with this expectation the triplet-sensitized decomposition of diastereoisomeric dimethylpyrazolines in solution [28] yields the diastereoisomeric dimethylcyclopropanes in an equal *cis*-to-*trans* ratio. Upon direct photolysis, however, this ratio is no longer equal for the two diastereoisomeric dimethylpyrazolines.

Accordingly, the oxirans appear to be formed as a singlet state species whereby a singlet alkyl oxyl 1,3 biradical and a hot ground state oxiran are taken to be conceptually equivalent. As well as the photolytic generation of

such species as in the present case, one envisages their formation via the addition of $O(^1D)$ atoms to olefins or in the pyrolysis of epoxides. Because these methods of energization differ the active species obtained are probably different in each case and caution must be exercised in the adduction of the results of these other techniques. In particular the question to be raised here is whether or not this species is also the precursor of 2-butanone, a product which could be rationalized by assuming a 1,2 hydrogen shift of the alkyl oxyl 1,3 biradical (hot ground state). It is well known that epoxides and carbonyl compounds are produced when $O(^1D)$ atoms react with olefins in the gas phase [29]. A recent study [30] of this subject has reached the conclusion that the carbonyl compounds in the olefin- $O(^1D)$ system do not arise from a 1,2 hydrogen shift of an intermediate oxygen atom adduct to the double bond but rather from an insertion into a vinylic hydrogen atom with subsequent enol \rightarrow keto rearrangement.

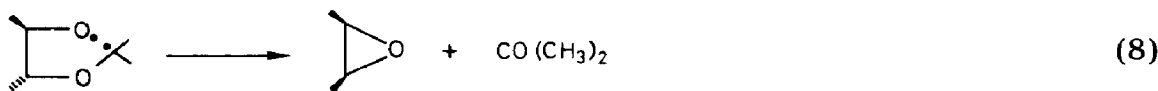
It was concluded from a pyrolysis study of *cis*- and *trans*-2,3-dimethyloxirans that the 1,2 hydrogen shift is faster than rotation and reclosure of the C-O bond [31]. When this is compared with the behaviour of 1,2-dimethylcyclopropane on pyrolysis, it can be seen that in the corresponding hydrocarbon 1,3 biradicals the 1,2 hydrogen shift is slower than rotation and reclosure [32]. If indeed the alkyl oxyl 1,3 biradical (hot ground state) undergoes the 1,2 hydrogen shift considerably faster than the alkyl alkyl 1,3 biradicals it is readily understandable that in the UV photolysis of tetrahydrofuran in the liquid state where such 1,3 biradicals (or hot three-membered-ring species) are also implicated barely any propene is found (the cyclopropane-to-propene ratio is about 30) whereas oxiran and acetaldehyde are formed with about equal yields [6].

In view of this it is likely that in the present system the 2-butanone is also formed by a 1,2 hydrogen shift. The intramolecular disproportionation reaction (5-3) (see Fig. 2) leading to the labile hemiacetal cannot be excluded, but preference is given to reaction (4) as the source of 2-butanone.

A stereoretentive route to dimethyloxiran that assumes a zwitterionic intermediate [33] could be postulated:



An S_R2 pathway through an alkyl oxyl 1,5 biradical



would lead to the inverted product which, however, is the minor product.

4.2. Inversions at C(2) and C(4)

The *cis*- and *trans*-2,2,4,5-tetramethyl dioxolans merely allow an inversion at C(4) to be monitored and, as expected, there is evidence for an inversion at this centre (see the last two products listed in Table 1). These educts, however, cannot indicate an inversion at C(2) of the dioxolane ring. With the introduction of a further stereochemical label such as that possessed by compounds 3 and 4 this becomes possible.

Figure 3 summarizes the expected inversions if the whole set of biradicals (6 - 9) are assumed to be intermediates. Educt 5 is a racemic mixture and for this reason we cannot detect the intermediacy of biradical 9. Conversion of 5 into 3 and 4 reflects the inversion at C(4). The data in Table 2 show that for these compounds scission followed by inversion is roughly the same for both kinds of radical centres.

The quantum yield of bond scission must exceed the quantum yield of inversion. This factor will be determined by the precursor multiplicity and the rates of inversion and reclosure, as well as by configurational preferences. These parameters are not yet known. Although the quantum yields in Table 2 appear to be small they gain in importance if we consider that, at a quantum yield of educt consumption of about 0.15, inversion reactions account for about 20% of the photochemistry.

The conclusion (which removes an apparent discrepancy between the photolytic behaviour of cyclic and acyclic acetals) is that in the 1,3-dioxolans not only the O(1)-C(5) bond is broken as had been suggested earlier [11], but also the O(1)-C(2) bond, and that the latter biradical appears to reclose efficiently without giving rise to other products.

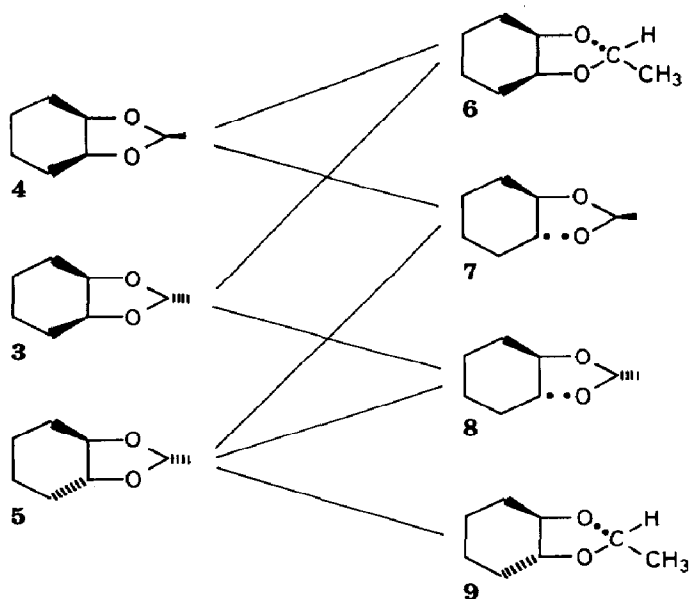


Fig. 3. Relationship between the diastereoisomeric cyclohexanodioxolans 3 - 5 and the corresponding alkyl oxyl 1,5 biradicals 6 - 9.

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