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PHOTOCHEMICALLY INITIATED REACTIONS OF SUBSTITUTED 1,3-DIOXOLANES AND 1,3-OXATHIOLANES IN $CFCl_3$

ESR STUDY AND MECHANISM OF RING-FISSION

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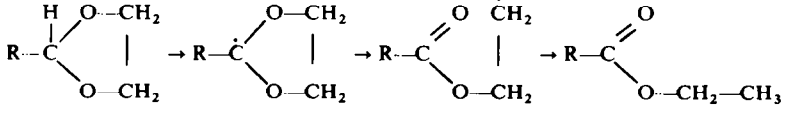
Abstract—The photochemical reactions of some 2-alkyl-1,3-dioxolanes and 2-alkyl-1,3-oxathiolanes in $CFCl_3$ in the presence of benzophenone yield exclusively the *open* 2-chloroethyl carboxylic esters and *S*-2-chloroethyl thiocarboxylic esters respectively. Photochemically excited benzophenone abstracts the hydrogen atom at carbon between the heteroatoms from the substrate to give intermediate *cyclic* (thio)acetal radicals which can be trapped efficiently by 2-nitroso-2-methylpropane in inert solvents. The resulting nitroxides are identified by their ESR hfs-constants. No ring-opened (thio)ester radicals could be trapped. The course of photolysis of optically active 2*RS*,4*R*-(—)-2-methyl-4-phenyl-1,3-dioxolane and other (racemic) 2,4-disubstituted-1,3-dioxolanes supports a mechanism in which a cyclic radical abstracts halogen from the solvent to form an intermediate cyclic chloro-(thio)acetal. Heterolytic cleavage of the new C—Cl bond gives the well stabilized cyclic carbonium ion and chloride anion. Nucleophilic attack of chloride ion at the C-4 or C-5 carbon atom (involving inversion for a chiral C-4) leads to ring rupture and formation of the final product.

INTRODUCTION

FREE radical reactions of acetals, induced by thermally generated alkoxy radicals[1–5] or by photoactivated ketones[6–8] have been studied by several groups of investigators. A variety of reactions has been detected, often involving hydrogen abstraction from the carbon adjacent to both oxygen atoms (as illustrated for 2-alkyl-1,3-dioxolane(I)) producing a cyclic acetal radical (II) which usually isomerizes to the ester radical (III). This ring-opened radical may abstract a hydrogen atom from the solvent to yield the carboxylic ester — (IV).*



I II III IV

Hydrogen abstraction at C-2 from 2,4-disubstituted-1,3-dioxolanes may result in β-scission to give predominantly the n-alkyl ester derived from the more stable

* These free radical reactions must be carried out under nitrogen, in the presence of oxygen mainly hydroperoxides are obtained.[8]

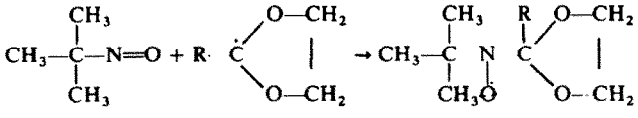
secondary radical.[3,8] In several cases cyclic acetal radicals have been trapped by alkenes to give the 1 :1 addition product, most efficiently by diethyl maleate under photolytic conditions; no trace of the ring-opened ester radical can be trapped in this case.[7] At higher temperatures both the cyclic radical and the ester radical are trapped by 1-octene.[4]

The purpose of the present investigation was twofold. First of all to study the effect of substituents in 1.3-dioxolanes and 1.3-oxathiolanes on the propensity for formation of open *versus* closed radicals by means of the ESR spin trapping technique[9,10] with 2-nitroso-2-methylpropane (V) as a scavenger. Secondly. to elucidate the reaction mechanism (homolysis and/or heterolysis) of the benzophenone-induced photochemical reactions of substituted 1.3-dioxolanes and 1.3-oxathiolanes in $CFCl_3$ as a solvent.

RESULTS AND DISCUSSION

An ESR study of radicals derived from substituted 1.3-*dioxolanes*

We have used 2-nitroso-2-methylpropane (V) as a highly efficient trap in the free radical reactions of a number of substituted 1.3-dioxolanes under various conditions. In benzophenone-induced photochemical reactions and in thermal reactions with t-butoxy radicals* as an initiator the same nitroxides (VI). derived from the *cyclic* acetal radicals are observed; these nitroxides are sufficiently stable to be studied at room temperature by ESR in C_6H_6 solution.



V (R=H. alkyl. aryl) VI

Especially under photochemical conditions the trapping agent itself gives rise to the formation of di-t-butyl nitroxide; the signal of this radical is sometimes so strong that the signal from VI is hardly visible.

The structures of the nitroxides (VI) are readily deduced from the observed hfs-constants. In most cases only a nitrogen splitting is observed with a_N values of 13–14 gauss (Table 1) which is somewhat lower than usually found in dialkyl nitroxides (a_N = 15–16 gauss). The slightly reduced spin density at nitrogen will be the result of the inductive effect of the oxygen atoms attached to the α-carbon atom.[12]

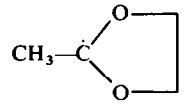
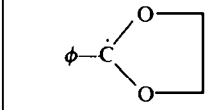
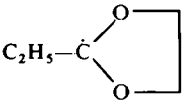
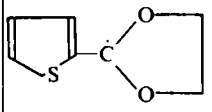
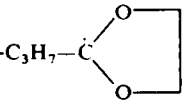
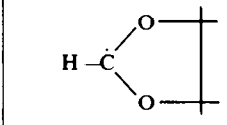
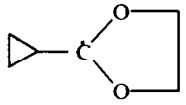
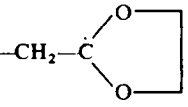
In C_6H_6 no nitroxides derived from the open ester radical were observed. not even when four Me groups are attached at C-4 and C-5 to facilitate the ring opening. The ESR spectrum of the nitroxide derived from 4.4.5.5-tetramethyl-1.3-dioxolane shows an additional splitting due to one β-hydrogen atom. as expected for the trapped cyclic radical.

In the case of unsubstituted 1.3-dioxolane a complex ESR spectrum is obtained. apparently due to nitroxides derived from a mixture of acetal radicals formed by hydrogen abstraction at C-2 and C-4†. Apparently, selective hydrogen abstraction at

* Formed by thermal decomposition of di-t-butyl peroxyoxalate (TBPO) at room temperature.[11]

† The non-specific hydrogen abstraction from this compound has been noted before.[4]

TABLE 1. HFS-CONSTANTS OF NITROXIDE RADICALS FORMED IN BENZENE AT 20° *via* HYDROGEN ABSTRACTION FROM CYCLIC AND ACYCLIC ACETALS IN THE PRESENCE OF 2-NITROSO-2-METHYLPROPANE

Trapped radical R$^{\cdot}$ from parent acetal RH	t-Bu(R)NO$^{\cdot}$ a_N (gauss)	Trapped radical R$^{\cdot}$ from parent acetal RH	t-Bu(R)NO$^{\cdot}$ a_N (gauss)	a_H (gauss)	
	14·1		14·1	—	
	13·9		14·0	—	
	14·1		13·2	0·94	(1H)
	14·1	$H-\dot{C}(OCH_3)_2$	13·5	1·9	(1H)
	13·8	$CH_3-\dot{C}(OCH_3)_2$	13·6	—	

C-2 only takes place when a substituent at this position provides extra stabilization of the radical.

In Table 1 ESR data of two nitroxides derived from acyclic acetals have been included for comparison. Again. the acetal radical can be trapped efficiently by 2-nitroso-2-methylpropane before the formation of the alkyl radical and the ester proceeds to a measurable extent.

The stability and geometry of oxygen-conjugated radicals is under active discussion in the recent literature.[13,14] Norman[15,16] has obtained strong evidence that these radicals possess a non-planar structure by measuring ^{13}C hfs-constants. It is interesting to note that for 2-cyclopropyl-1.3-dioxolane only the ESR spectrum from a nitroxide with an intact cyclopropyl ring is observed. This is somewhat surprising because α-cyclopropyl carbinyl radicals usually undergo a rapid ring opening* unless there is strong resonance stabilization of the radical center.[18,19] It may be tentatively proposed that the decreased propensity for cyclopropyl ring opening for the radical derived from 2-cyclopropyl-1.3-dioxolane might be the result of a non-planar geometry. In the following section the photolyses of some substituted 1.3-dioxolanes in the chlorine-donating solvent $CFCl_3$ are described. Although ring-opened products are finally obtained. we will show that in agreement with the ESR experiments. no

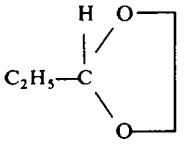
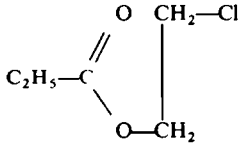
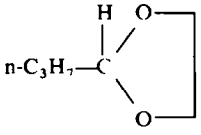
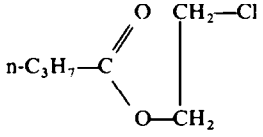
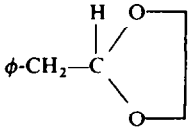
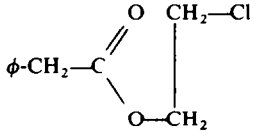
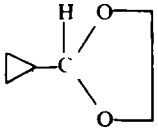
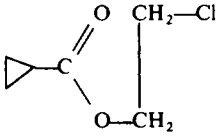
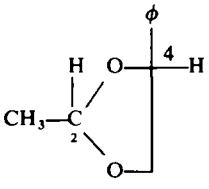
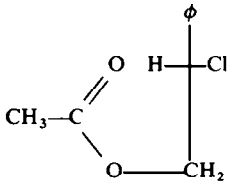
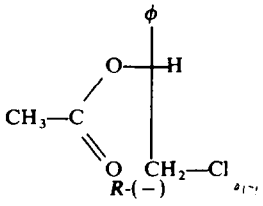
* The cyclopropyl carbinyl radical is stable at −150° and gives β-scission at −100° to form the allyl carbinyl radical.[17]

ring-opened radicals are involved in the photochemically initiated reactions of 1.3-dioxolanes.

Reactions of substituted 1.3-*dioxolanes with excited benzophenone in* $CFCl_3$

The photochemically induced reactions of four 2-alkyl-1.3-dioxolanes were studied in $CFCl_3$ as solvent* with benzophenone as initiator† (Table 2). In all cases

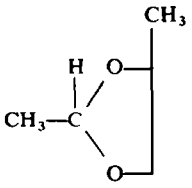
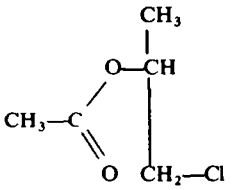
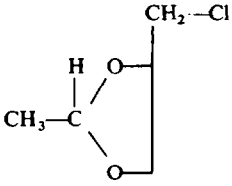
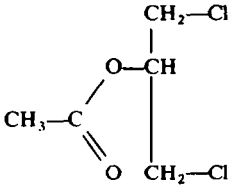
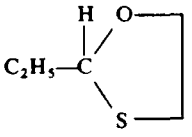
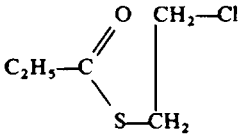
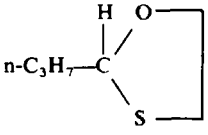
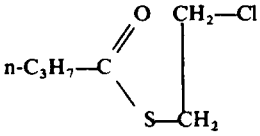
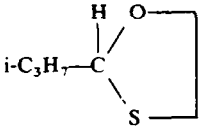
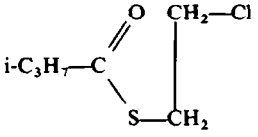
TABLE 2. PHOTOLYSES OF SUBSTITUTED 1,3-DIOXOLANES AND 1,3-OXATHIOLANES IN $CFCl_3$ IN THE PRESENCE OF BENZOPHENONE.

Starting material	Reaction product(s)	Yield (%)	b.p.	NMR spectral data[a]
			67–69 /30 mm	1·16 t. 3H . 2·38 (q. 2H).
		35	67–69°/30 mm	1·16 (t, 3H). 2·38 (q. 2H), 3·70 (t, 2H). 4·34 (t. 2H)
		62	74–76°/30 mm	0·95 (t. 3H). 1·65 (m. 2H). 2·38 (t. 2H). 3·64 (t. 2H) 4·26 (t. 2H)
		54[b]	160°/15 mm	3·58 (t, 2H). 3·63 (s. 2H). 4·29 (t. 2H). 7·29 (s. 5H)
		50	41–42°/4 mm	0·91 (m. 4H). 1·60 (m. 1H). 3·63 (t. 2H). 4·27 (t. 2H)
 2*RS*. 4*R*-(−)[c,d]	 *S*-(+)	52·6[d]	113–115°/2 mm	2·02 (s. 3H). 4·45 (d. 2H). 5·09 (t. 1H). 7·38 (s. 5H)
	 *R*-(−)	4·0[d]	119°/1·5 mm	2·09 (s. 3H). 3·74 (d. 2H). 6·00 (t. 1H). 7·36 (s. 5H)

* All studies reported in the literature have been performed in hydrogen donating media, either the pure 1.3-dioxolane itself or with an alcohol as solvent.

† No reaction occurred in the absence of benzophenone; benzpinacol was found as a byproduct.

TABLE 2—*continued*

Starting material	Reaction product(s)	Yield (%)	b.p.	NMR spectral data[a]
		49	47–51°/15 mm	1·33 (d. 3H). 2·05 (s. 3H), 3·57 (d. 2H). 5·13 (m. 1H)
		44	97–98°/22 mm	2·13 (s. 3H). 3·75 (d. 4H). 5·18 (qnt, 1H).
		22[b,d]	82°/15 mm	1·19 (t. 3H). 2·58 (q. 2H). 3·17 and 3·58 A_2B_2, 4H)
		38[b,d]	90°/16 mm	0·95 (t. 3H). 1·69 (m. 2H). 2·58 (t. 2H). 3·23 and 3·53 (A_2B_2. 4H)
		14[b,d]	88°/15 mm	1·18 (d. 6H). 2·75 (spt. 1H). 3·17 and 3·62 A_2B_2, 4H

[a] Chemical shifts in ppm (δ-values). Spectra of *S*-2-chloroethyl thioesters in CCl_4; the other spectra in $CDCl_3$. s = single d = doublet. t = triplet. q = quartet. qnt = quintet. spt = septet. m = multiplet.

[b] Yield based on consumed starting material.

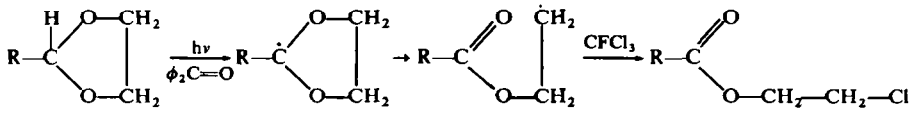
[c] Specific rotations of starting material and products: *cf.* Experimental.

[d] New compounds.

a smooth conversion into a 2-chloroethyl carboxylic ester (VII) is observed. This can be explained by either of the following mechanisms (A and B).

The ESR study did not provide any evidence for β-scission of cyclic acetal radicals (II) and this renders mechanism A (Scheme 1) *a priori* improbable.

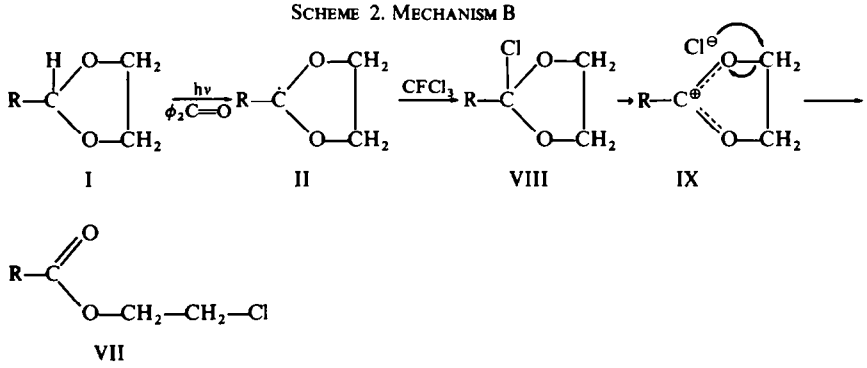
SCHEME I. MECHANISM A (HYPOTHETICAL)



I II III VII

In mechanism B the formation of a 2-chloro-2-alkyl-1.3-dioxolane (VIII) is assumed. apparently *via* abstraction of a Cl atom from the solvent by the *cyclic* acetal radical (II).

SCHEME 2. MECHANISM B



I II VIII IX

VII

Such cyclic chloro-acetals are known to be very reactive species which have never been isolated. Although Baker *et al.*[20] reported the preparation of 2-chloro-1.3-dioxolane by photochemical chlorination of 1.3-dioxolane. Bagans *et al.*[21] repeated this experiment more recently and isolated only the isomeric 2-chloroethyl formate. One cyclic chloro-acetal (*i.e.* 2-chloro-2-dichloromethyl-1.3-dioxolane) has been prepared* at $-60°$ as judged by its low-temperature NMR spectrum.[23]

Since a carbonium ion is strongly stabilized by two neighbouring oxygen atoms the chloro-acetal VIII will easily give heterolytic cleavage of the C—Cl bond. The oxygen atoms with fractional positive charges will facilitate an S_N2 reaction of chloride ion at the neighbouring C-4 carbon atom to yield 2-chloroethyl carboxylic ester (VII). (Scheme 2).

In order to substantiate the occurrence of mechanism B the photolyses of some appropriately substituted chiral 1.3-dioxolanes were carried out in $CFCl_3$ (Table 2). For this purpose we synthesized optically active 2*RS*.4*R*-(−)-2-methyl-4-phenyl-1.3-dioxolane (X). Starting material was *R*-(−)-mandelic acid; reduction with $LiAlH_4$ yielded *R*-(−)-1-phenyl-ethane-1.2-diol (XIII). Acid catalyzed reaction of XIII with acetaldehyde afforded 2*RS*.4*R*-(−)-2-methyl-4-phenyl-1.3-dioxolane (X). X was optically pure.† because acid catalyzed hydrolysis yielded *R*-(−)-XIII with nearly the same rotation as the starting diol (Scheme 3).

This shows *inter alia* that a carbonium ion is stabilized much better by a neighbouring oxygen atom than by a Ph group. because rupture of the O-3—C-4 bond would have caused a fair amount of racemization.

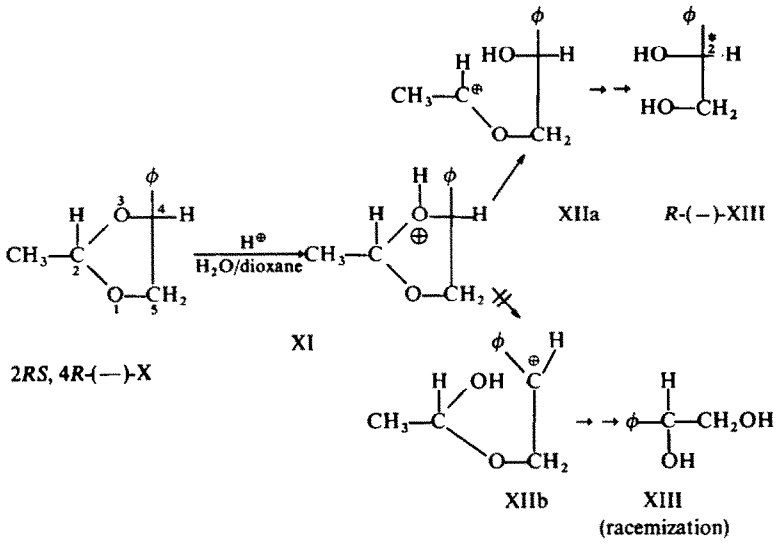
Stereochemistry of ester formation

When 2*RS*.4*R*-(−)-2-methyl-4-phenyl-1.3-dioxolane (X) is photolysed in the presence of benzophenone in $CFCl_3$. *S*-(+)-2-acetoxy-1-chloro-1-phenylethane (XVII) and *R*-(−)-1-acetoxy-2-chloro-1-phenylethane (XVIII) are formed in a ratio

* A few open chloro-acetals have been prepared *via* other routes.[22]

† Optically pure at chiral center C-4. In practice X is a mixture of diastereoisomers due to the other asymmetric center C-2. However. the configuration of C-2 is not relevant in the mechanism of the photolysis of X.

SCHEME 3. HYDROLYSIS OF OPTICALLY ACTIVE X*



93:7. Both products are new compounds and were also synthesized *via* independent routes (*cf.* Experimental).

The β-chloro-ester XVII was found to be formed with 100% inversion of configuration. This strongly suggests that an S_N2 reaction has occurred at C-4; this is in agreement with the mechanism involving the cyclic chloro-acetal XV (Scheme 4).† Since the carbonium ion in XVI is so well stabilized by two neighbouring oxygens. it has no tendency for heterolytic scission of the O-3—C-4 bond to form a (planar) benzylic carbonium ion and this explains why no racemic XVII is found. Apparently the only possibility for heterolytic ring opening is a simultaneous attack of the chloride ion at C-4 to produce XVII with inversion of configuration.

Chiral center C-4 is not involved in the reaction leading to compound XVIII. which is therefore formed with retention of configuration.

When the Ph group in X is replaced by Me or chloromethyl as in XIX. the chloride ion attacks the least substituted position in the intermediary carbonium ion to give the ester XXI. while the isomeric ester derived from chloride attack at C-4 is not formed at all.

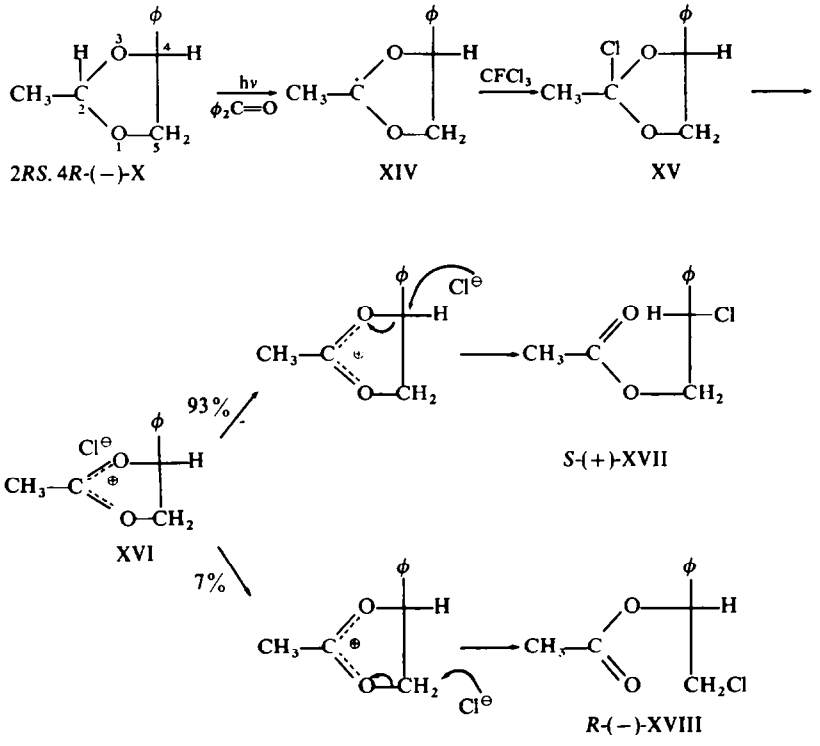
Apparently steric factors are relatively important. whereas in the case with a Ph substituent electronic factors determine the product selectivity.

The same type of selectivity was recently reported by Gelas *et al.*[24] for the reaction of 2.4-dialkyl-1.3-dioxolanes with N-bromosuccinimide; again only the least substituted position (C-5) is attacked (by bromide) to form a bromo ester analogous to XXI. The formation of a cyclic bromo-acetal followed by heterolytic ring opening (S_N2) might well explain these experimental results.

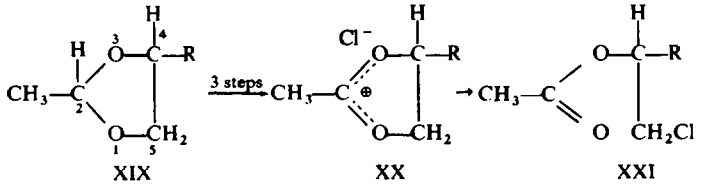
* Only protonation of the O-3 oxygen atom is exemplified in this scheme.

† Our experimental data do not provide information about the details of the formation of XVI from XIV. The sequence depicted in Scheme 4, *i.e.* chlorine abstraction from the solvent to give XV followed by ionization to XVI seems plausible.

SCHEME 4. PHOTOLYSIS OF OPTICALLY ACTIVE X



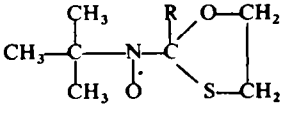
SCHEME 5. PHOTOLYSIS OF 2,4-DIALKYL-1,3-DIOXOLANES



R = CH_3, CH_2Cl

Radical reactions of 2-alkyl-1.3-oxathiolanes

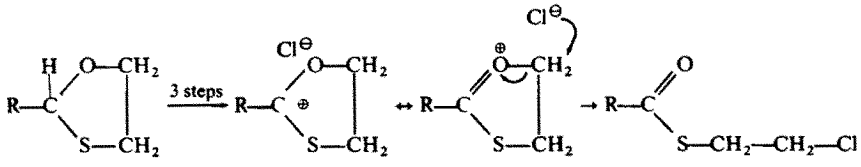
Cyclic thioacetal radicals can be generated by hydrogen abstraction at C-2 from 2-alkyl-1.3-oxathiolanes (XXIII) by t-butoxy radicals. Trapping with 2-nitroso-2-methylpropane produces nitroxides (XXII); the a_N values of these radicals are in the same range as those derived from cyclic acetal radicals (Table 3). We have photolysed



XXII

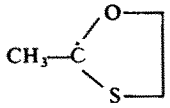
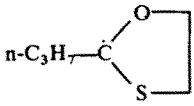
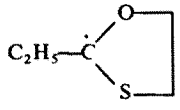
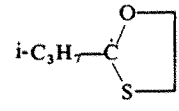
several 2-alkyl-1.3-oxathiolanes (XXIII) in $CFCl_3$ in the presence of benzophenone (Table 2). The reactions are considerably slower than the photolyses of 2-alkyl-1.3-dioxolanes when carried out under similar experimental conditions and are highly selective. Only the *S*-2-chloroethyl thioester (XXV) and no trace of the *O*-2-chloroethyl thioester is formed. Assuming a similar mechanism for the photolyses of 2-alkyl-1.3-oxathiolanes as for substituted 1.3-dioxolanes. the observed reaction products can be explained by the fact that a carbonium ion is much better stabilized by a neighbouring oxygen than by a neighbouring sulfur atom.[25] Therefore resonance structure XXIVb is the more important. which makes the carbon atom attached to oxygen more susceptible to nucleophilic attack than the carbon atom attached to sulfur.

SCHEME 6. PHOTOLYSIS OF 2-ALKYL-1,3-OXATHIOLANES



Another factor which may contribute to the observed specific ring opening is the higher stability of *S*-alkyl thioesters as compared with *O*-alkyl thioesters.[26]

TABLE 3. HFS-CONSTANTS OF NITROXIDE RADICALS FORMED IN BENZENE AT 20° *via* HYDROGEN ABSTRACTION FROM 2-ALKYL-1,3-OXATHIOLANES IN THE PRESENCE OF 2-NITROSO-2-METHYLPROPANE

Trapped radical R$^{\cdot}$ from parent acetal RH	t-Bu(R)NO$^{\cdot}$ a_N (gauss)	Trapped radical R$^{\cdot}$ from parent acetal RH	t-Bu(R)NO$^{\cdot}$ a_N (gauss)
	14·4		14·3
	14·3		14·3

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were recorded with a Unicam SP200 spectrometer. NMR spectra were determined on a Varian A-60 or A-60D instrument using TMS as internal standard ($\delta = 0$) and $CDCl_3$ or CCl_4 as solvent. Optical rotations were measured on a Zeiss LEP polarimeter in a 1 dm tube at 20°. concentrations are in g/100 ml. ESR spectra were taken on a Varian E-3 apparatus fitted with an optical transmission cavity; the light source was a Philips SP 500 W super high pressure mercury lamp. A similar light source was used for the photolyses. carried out under N_2 at 0° in Pyrex with stirring. Microanalyses were carried out by Mr. H. Pieters in our laboratory.

All 2-alkyl-1.3-dioxolanes and 2,4-dialkyl-1.3-dioxolanes were prepared from the corresponding aldehydes and diols. using *p*-TsOH as catalyst and C_6H_6 as solvent; H_2O was removed azeotropically.

All 2-alkyl-1.3-oxathiolanes were prepared in a similar way from the aldehydes and 2-mercapto-ethanol. 4.4.5.5-Tetramethyl-1.3-dioxolane was prepared according to Leutner.[27]

2RS.4R-(−)-2-methyl-4-phenyl-1.3-dioxolane (X). Reduction of 10·0 g of *R*-(−)-mandelic acid* in 300 ml dry ether with 6·5 g of LAH in 150 ml of ether gave 6·1 g *R*-(−)-1-phenylethane-1.2-diol. crystallized from ether-light petroleum 1 : 1 m.p. 66·0–68·5°, $[\alpha]_D$ − 42·0° (*c.* 6·5 96% EtOH).

Water was removed azeotropically from a mixture of 5·8 g of *R*-(−)-1-phenylethane-1.2-diol. 1·84 g of paraldehyde. 0·20 g of *p*-TsOH and 150 ml of C_6H_6 during 3 hr. After drying (K_2CO_3) and removal of solvent. distillation afforded 5·1 g *2RS.4R*-(−)-2-methyl-4-phenyl-1.3-dioxolane. b.p. 115–116°/21 mm. $[\alpha]_D$ − 69·5°. $[\alpha]_{578}$ − 73·1° (*c.* 2·4. cyclohexane); (Found: C. 73·10; H. 7·49; $C_{10}H_{12}O_2$ requires: C. 73·15; H. 7·37%).

Photolyses of substituted 1.3-dioxolanes and 1.3-oxathiolanes. A uniform procedure was used for the photolyses of all substituted 1.3-dioxolanes and 1.3-oxathiolanes as exemplified for 2-cyclopropyl-1.3-dioxolane.

A mixture of 3·0 g of 2-cyclopropyl-1.3-dioxolane. 7·5 g of benzophenone and 200 ml of dry $CFCl_3$ was deoxygenated and irradiated for 17 hr at 0°. Solvent was evaporated at atmospheric pressure (some HCl also evolved) and the residue distilled under reduced pressure. yielding 1·95 g 2-chloroethyl ester of cyclopropane carboxylic acid b.p. 41–42°/4 mm. A second fraction. b.p. 124–125°/4 mm. solidified and proved to be unreacted benzophenone. In some cases a small amount of precipitate was formed during the photolysis; this was shown to be benzpinacol.

The photolyses of the 1.3-oxathiolanes proceeded slower and some starting material was always recovered after the photolyses. The resulting (thio)esters were purified by GLC. All spectral data were in accordance with proposed structures (Table 2). The *new* *S*-2-chloroethyl thioesters were also characterized by their microanalyses:

S-2-chloroethyl thiopropionate (Found: C. 39·31; H. 6·04; Cl. 23·06; S. 20·90; C_5H_9ClOS requires: C. 39·34; H. 5·94; Cl. 23·23; S. 21·01%).

S-2-chloroethyl thiobutyrate (Found: C. 43·46; H. 6·72; Cl. 21·15; S. 19·07; $C_6H_{11}ClOS$ requires: C. 43·24; H. 6·65; Cl. 21·27; S. 19·24%).

S-2-chloroethyl thioisobutyrate (Found: C. 43·17; H. 6·76; Cl. 21·24; S. 19·18; $C_6H_{11}ClOS$ requires: C. 43·24; H. 6·65; Cl. 21·27; S. 19·24%).

Hydrolysis of 2RS,4R-(−)-2-methyl-4-phenyl-1.3-dioxolane (X). Compound X (0·6 g) was hydrolysed in a mixture of 30 ml 10% H_2SO_4 and 5 ml of dioxane. 3 hr at 50°. The solution was extracted three times with 40 ml portions of ether; drying (K_2CO_3) and evaporation of solvent yielded 0·12 g *R*-(−)-1-phenylethane-1.2-diol with $[\alpha]_D$ − 40·2° (*c.* 1·2. 96% EtOH).

Photolysis of 2RS.4R-(−)-2-methyl-4-phenyl-1.3-dioxolane (X). Compound X (4·3 g). benzophenone (8·0 g) and 160 ml of $CFCl_3$ were irradiated under N_2 for 24 hr at 0°. After removal of solvent. the residue was distilled under reduced pressure; main fraction b.p. 102–105°/1 mm. 2·0 g. It was concluded from the NMR spectra that apart from unreacted X and benzophenone only two products were formed; the yields of *S*-(+)-2-*acetoxy*-1-*chloro*-1-*phenylethane* (XVII) and *R*-(−)-1-*acetoxy*-2-*chloro*-1-*phenylethane* (XVIII) were 52·6 and 4·0% respectively (ratio 93 : 7): *cf.* Scheme 4 and Table 2. Both XVII and XVIII are *new* compounds and were synthesized *via* independent routes to determine their specific rotations: $[\alpha]_{578}$ + 97·1° and − 77·3° respectively (in cyclohexane). The main fraction obtained by photolysis of X consisted of 5% X. 73% XVII. 5% XVIII and 18% benzophenone. as determined by NMR. The observed rotation of this mixture at 578 nm was + 5·60° (*c.* 8·55. cyclohexane; *l*, 1 dm). This rotation is the sum of the rotations of X. XVII and XVIII. Since we are only interested in the rotation of XVII we have to make corrections for the presence of small amounts of X and XVIII. These two however. are present in their optical pure form (the former is starting material and chiral center C-4 is not involved in the formation of the latter) and their "sub-concentrations" can easily be calculated; the rotations at 578 nm are − 0·28° and − 0·33° respectively.

The value for α_{578} is therefore + 6·21° for XVII; the sub-concentration is 6·23. so $[\alpha]_{578}$ is + 99·7° (cyclohexane). Since the specific rotation of optically pure XVII is $[\alpha]_{578}$ + 97·1°. XVII is formed during the photolysis with 100% inversion of configuration.

Synthesis of S-(+)-2-acetoxy-1-chloro-1-phenylethane (XVII). *S*-(+)-mandelic acid was treated with

* Commercial sample of 97·6% optical purity: a correction factor of 1·025 has therefore been applied in calculating specific rotations of derivatives.

† Values of 67–68° and + 40·6° are reported for the enantiomer.[28]

$SOCl_2$ according to McKenzie and Barrow[29] yielding *S*-(+)-phenyl chloroacetic acid with $[\alpha]_{578}$ + 113·5° (*c.* 0·8. C_6H_6); optical purity 60%.*

A solution of B_2H_6 (2·0 g) in THF (25 ml) was added at 0° to a solution of 3·3 g of *S*-(+)-phenyl chloroacetic acid in dry THF (40 ml). The mixture was refluxed for 1 hr and poured into ice-water. After saturation with NaCl the mixture was extracted with ether; drying ($MgSO_4$) and evaporation of solvent afforded 3·0 g crude *S*-(+)-2-chloro-2-phenylethanol. The NMR spectrum did not reveal the presence of other compounds and the product was used without purification.

Freshly distilled acetyl chloride (8 ml) in cyclopentane (8 ml) was added in 15 min to a refluxing solution of 2·7 g of *S*-(+)-2-chloro-2-phenylethanol in cyclopentane (10 ml); the mixture was refluxed for another 5 hr and poured into ice-cold $NaHCO_3$ aq. Extraction with ether. drying ($MgSO_4$). removal of solvent and distillation gave 2·1 g *S*-(+)-2-*acetoxy*-1-*chloro*-1-*phenylethane*. b.p. 113–115°/2 mm. $[\alpha]_{578}$ + 58·0° (*c.* 5·0. cyclohexane). For spectral data: *cf.* Table 2. (Found: C. 60·59; H. 5·46; Cl. 17·66; $C_{10}H_{11}ClO_2$ requires: C. 60·46; H. 5·58; Cl. 17·85%). Since the optical purity of the *S*-(+)-phenyl chloroacetic acid was 60% the specific rotation of optically pure XVII will be $[\alpha]_{578}$ + 97·1°. $[\alpha]_D$ + 93·0°.

Synthesis of R-(−)-1-acetoxy-2-chloro-1-phenylethane (XVIII). Racemic 2-chloro-1-phenylethanol was prepared according to Sumrell *et al.*[31] Equimolar amounts of 2-chloro-1-phenylethanol. phthalic anhydride and py. was heated at 110° for 2 hr; the mixture was poured into dilute HCl; extraction with $CHCl_3$. drying ($MgSO_4$) and evaporation of solvent yielded the hydrogen phthalate of (racemic) 2-chloro-1-phenylethanol. crystallized from C_6H_6-light petroleum 1:1. m.p. 91·5–92·5°; 87%.

The brucine salt of this hydrogen phthalate was resolved by fractional crystallization from acetone. The less soluble salt was recrystallized five times until the specific rotation and m.p. were constant: $[\alpha]_{364}$ − 50·8° (*c.* 2·1. 96% EtOH). m.p. 126–128°. white needles. Treatment with dilute HCl. extraction with ether. washing with very dilute HCl. drying ($MgSO_4$) and removal of solvent yielded the optically pure hydrogen phthalate of (−)-2-chloro-1-phenylethanol. obtained as a very viscous oil.† dextrorotatory (in EtOH). Possibly the solvent was not removed completely. thus the calculated specific rotation might not be accurate: $[\alpha]_{364}$ + 78·7° (*c.* 3·0. 96% EtOH).

The normal procedure to convert hydrogen phthalates of optically active alcohols into the alcohols without racemization is saponification with simultaneous steam distillation.[32] This procedure fails in our case. because only epoxyethylbenzene is formed under the basic conditions. However. this reaction was favorably used to establish the absolute configuration of the hydrogen phthalate of (−)-2-chloro-1-phenylethanol and derivatives. A solution of 0·5 g of NaOH in boiling water (30 ml) was added to 1·0 g of the hydrogen phthalate; steam distillation was carried out immediately. the distillate extracted with ether. dried ($MgSO_4$) and solvent evaporated to give 0·24 g of optically active epoxyethylbenzene. $[\alpha]_D$ + 3·8° (*c.* 1·2, cyclohexane); (+)-epoxyethylbenzene is known to have the *R*-configuration.[33, 34] The hydrogen phthalate of (−)-2-chloro-1-phenylethanol also has the *R*-configuration since *R*-(+)-epoxyethylbenzene is formed with retention of configuration in the saponification reaction.

The following method was used to convert the optically pure hydrogen phthalate into *R*-(−)-2-chloro-1-phenylethanol. A solution of B_2H_6 (4·4 g) in THF (55 ml) was added at 0° to a solution of 6·2 g of the hydrogen phthalate in dry THF (40 ml). The mixture was refluxed for 1 hr and then poured into ice-water. After saturation with NaCl the mixture was ether extracted; drying ($MgSO_4$) and evaporation of solvent gave a residue consisting of only *R*-(−)-2-chloro-1-phenylethanol and phthalyl alcohol. The former was isolated by distillation. 2·35 g. b.p. 119–120°/11 mm. $[\alpha]_D$ − 47·8° (*c.* 2·8. cyclohexane); spectra of this *new* compound were identical with those obtained from racemic material.

Freshly distilled acetyl chloride (9 ml) in 8 ml of cyclopentane was added to a refluxing solution of 2·0 g of *R*-(−)-2-chloro-1-phenylethanol in cyclopentane (20 ml); the mixture was refluxed for 12 hr. Excess acetyl chloride and solvent were evaporated. ether added to the residue and the solution washed with $NaHCO_3$ aq and H_2O; drying ($MgSO_4$). removal of solvent and distillation produced 1·9 g of *R*-(−)-1-*acetoxy*-2-*chloro*-1-*phenylethane* (XVIII), b.p. 119°/1·5 mm. $[\alpha]_{578}$ − 77·3°, $[\alpha]_D$ − 73·6° (*c.* 2·9, cyclohexane). For spectral data: *cf.* Table 2. (Found: C. 60·58; H. 5·62; Cl. 18·02; $C_{10}H_{11}ClO_2$ requires: C. 60·46; H. 5·58; Cl. 17·85%).

ESR of 1,3-dioxolanes. Optimal results are obtained when equal amounts of a substituted 1,3-dioxolane and di-t-butyl peroxyoxalate[11] (TBPO) are dissolved in a dilute solution of 2-nitroso-2-methylpropane

* $[\alpha]_{578}$ is reported to be −190° for the pure enantiomer.[30]

† A sample of this oil was kept for several weeks at room temperature and solidified to a crystalline mass. m.p. 71–72°.

(t-BuNO) in C_6H_6 (roughly 5 mg per ml). TBPO decomposes slowly at room temperature and immediately the nitroxide (VI) derived from the trapped acetal radical is observed; sometimes a small signal due to di-t-butyl nitroxide (a_N 15·5 gauss) is also present. Photolysis of the same sample produces large amounts of this nitroxide which obscures the signal derived from VI. However, in some cases, the nitroxides derived from the cyclic acetal radicals (VI) could be observed in photochemical benzophenone-induced reactions using very short (10 sec.) irradiation times.

ESR of 1.3-*oxathiolanes.* Similar results are obtained with 1.3-oxathiolanes using the TBPO method. Nitroxides (XXII) derived from the trapped thioacetal radicals are observed; sometimes small signals due to (unidentified) impurities are also present in the spectra. No radicals of type XXII could be detected during brief photolysis in a benzophenone-induced reaction; only di-t-butyl nitroxide was observed. Presumably photosensitized abstraction of the hydrogen at C-2 is a more difficult process in substituted 1.3-oxathiolanes as compared with substituted 1.3-dioxolanes.

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REFERENCES

[1] L. P. Kuhn and C. Wellman, *J. Org. Chem.* **22**, 774 (1957)
[2] E. S. Huyser, *Ibid.* **25**, 1820 (1960)
[3] E. S. Huyser and Z. Garcia, *Ibid.* **27**, 2716 (1962)
[4] B. Maillard, M. Cazaux and R. Lalande, *Bull. Soc. Chim. Fr* 467 (1971)
[5] P. Marche and D. Lefort, *C.R. Acad. Sci. Paris Ser.* C **269**, 717 (1969)
[6] D. Elad and R. D. Youssefyeh, *Tetrahedron Letters* 2189 (1963)
[7] I. Rosenthal and D. Elad, *J. Org. Chem.* **33**, 805 (1968)
[8] H. E. Seyfarth, A. Hesse and H. Pastohr, *Z. Chem.* **9**, 150 (1969)
[9] J. W. Hartgerink, J. B. F. N. Engberts, Th. A. J. W. Wajer and Th. J. de Boer, *Rec. Trav. Chim.* **88**, 481 (1969)
[10] C. Lagercrantz and S. Forshult, *Acta Chem. Scand.* **23**, 811 (1969)
[11] P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.* **82**, 1762 (1960)
[12] I. H. Leaver and G. Caird Ramsey, *Tetrahedron* **25**, 5669 (1969)
[13] A. Ohno and Y. Ohnishi, *Tetrahedron Letters* 4405 (1969)
[14] A. Hudson and K. D. J. Root, *Tetrahedron* **25**, 5311 (1969)
[15] A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *Chem. Comm.* 1353 (1969)
[16] R. O. C. Norman, *Chem. in Brit.* **6**, 66 (1970)
[17] J. K. Kochi, P. J. Krusic and D. R. Eaton, *J. Am. Chem. Soc.* **91**, 1877 (1969)
[18] D. C. Neckers, A. P. Schaap and J. Hardy, *Ibid.* **88**, 1265 (1966)
[19] J. C. Martin, J. E. Schultz and J. W. Timberlake, *Tetrahedron Letters* 4629 (1967)
[20] W. Baker and A. Shanon, *J. Chem. Soc.* 1598 (1933)
[21] H. Bagans and L. Domaschke, *Chem. Ber.* **91**, 653 (1958)
[22] J. W. Scheeren, *Tetrahedron Letters* 5613 (1968)
[23] H. Gross, J. Freiberg and B. Costisella, *Chem. Ber.* **101**, 1250 (1968)
[24] J. Gelas and S. Michaud, *C.R. Acad. Sci. Paris Ser.* C **270**, 1614 (1970)
[25] C. C. Price and S. Oae, *Sulfur Bonding* p. 10. Ronald Press, New York (1962)
[26] T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworths, London (1958)
[27] R. Leutner, *Monatsh. Chem.* **66**, 222 (1935)
[28] V. Prelog, M. Wilhelm and D. Bruce Bright, *Helv. Chim. Acta* **37**, 221 (1954)
[29] A. McKenzie and F. Barrow, *J. Chem. Soc.* 1910 (1911)
[30] K. Freudenberg, J. Todd and R. Seidler, *Liebigs Ann.* **501**, 199 (1933)
[31] G. Sumrell, B. M. Wyman, R. G. Howell and M. C. Harvey, *Can. J. Chem.* **42**, 2896 (1964)
[32] R. H. Pickard and J. Kenyon, *J. Chem. Soc.* 45 (1911)
[33] I. Tömösközi, *Tetrahedron* **19**, 1969 (1963)
[34] C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.* **90**, 6852 (1968)