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PHOTOCHEMICAL REACTION OF ALCOHOLS—II

IRRADIATION OF AROMATIC ALCOHOLS

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Abstract—The UV irradiation of aromatic alcohols leads to the formation of several products: carbonyl compounds, ethers, α-glycols and *tetra*-aryl-1,4-dioxanes.

The photoformation of α-glycols is qualitatively and quantitatively compared to the photoreduction of the carbonyl compounds. It is noteworthy that the glycols are formed with a stereochemistry very different depending upon whether the substrate is an alcohol or a carbonyl compound.

The structure, configuration and conformation of the 1,4-dioxanes obtained are studied as well as their origin.

Other aspects of the photochemistry of the alcohols are analyzed using hydroperoxides as model substrates.

We have previously reported[1] that by UV irradiation of aliphatic alcohols it was possible to obtain α-glycols as the main photoproducts.

Taking into account these results, we believed that to study the photochemical reaction of aromatic alcohols like Ar-RCH-OH should be interesting.

The aromatic alcohols were irradiated in methylene chloride solution employing a high pressure Hg lamp. Our first experiments indicated that the reaction was more complex than the photoreaction of aliphatic alcohols; the products obtained and their yields are given in Table 1.

The irradiation of phenylmethanol was the only experiment in which all the products indicated were obtained while in other experiments they were not simultaneously formed. The α-glycols are usually not the principal products because the original hydroxyalkyl radicals are not formed or because the glycols are able to be transformed to 1,4-dioxanes.

The principal products of these reactions, ethers and 1,4-dioxanes, had not been obtained by a photochemical method.

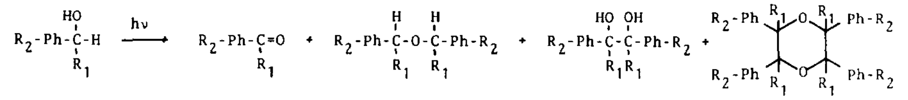
Phenylmethanol has been irradiated previously by Leuschner[2] who describes *meso*-1,2-*di*phenyl-1,2-ethanediol as the only product. This author mentions neither the *dl*-glycol nor *di*benzyl ether and the 1,4-dioxanes as products of the reaction.

Taking into account the mechanistic aspects of these reactions, the aromatic alcohols could be divided in two groups. The first one (phenylmethanol, (2-Cl-phenyl)- and (2-MeO-phenyl)methanol) has a photoreactivity similar to that of the aliphatic alcohols (see Mechanism of the photochemical reactions of the alcohols). In the second group the ethers and carbonyl compounds are the principal products; these results are typical of thermal reactions of aromatic alcohols.

Only one dioxane has been reported[3] which was obtained by heating phenylmethanol with P_4O_{10} but its structure was only assigned on the basis of microanalysis data.

The physical and spectroscopical properties (Tables 4 and 9) used for the determination of the dioxane structures will be analyzed later.

Table 1. Products obtained by UV irradiation of aromatic alcohols (yield[a]%)



R_1	R_2	conv.%	%	%	(dl+meso) %	%
H	H	66	2	6	2	88[b]
H	2-Cl	53	4	-	11	38[b]
H	2-MeO	60[c]	53	-	26	-
H	4-MeO	50	1	77	6	-
Me	H	31	3	60[d]	10	-
Et	H	32	13	79[d]	-	-
Ph	H	79	6	94	-	-
Ph	4-NO_2	89	99	-	-	-

a) yields were calculated from converted substrate.
b) this value corresponds to the diastereomers mixture. For phenylmethanol the ratio between the 1,4-dioxanes (XIII/XIV) was 0.27 and for 2-Cl-phenylmethanol (XV/XVI) it was 3.72.
c) the same irradiation performed under N_2 gave the following results: alcohol conv. 21%, α-glycols 18% and aldehyde 74%. On the other hand when in the original solution $NaBH_4$ (200 mg) was added, the yields obtained were: alcohol conv. 24% and α-glycols 75%.
d) diastereomers ratio: 1/1 (GLC analysis).

The α-glycols were identified (Table 3, MS)[a] from their physical properties or by comparison with authentic samples prepared by thermal methods (Experimental). The configurations of α-glycols were determined as we previously described[1] and were also confirmed by tlc (Table 3) because the R_f value of the *dl*-isomer was always higher than that corresponding to the *meso*-isomer.

The simplicity and resolution of ^{1}H-NMR spectra of the α-glycols should indicate that each diastereomer exists in only one conformation in which the bulky aryl groups are in position *anti.*

The aromatic α-glycols can also be obtained by photoreduction of carbonyl compounds. We performed these irradiations to compare both processes qualitatively and quantitatively.

The possibility that 1,1'-*di*aryl methyl ethers (Table 2) were formed through a dark reaction was discarded after studying the thermal stability of aromatic alcohols (Experimental).

The ethers coming from 1-phenylethanol and 1-phenyl-1-propanol were a mixture of diastereomers as it could be observed by glc analysis and ^{1}H-NMR spectroscopy.

Finally the description of Table 1 is completed saying that in two examples the carbonyl compound was the most important ((2-MeO-phenyl)-methanol)[b] or the sole product isolated (4-NO_2-*di*phenylmethanol).

Photochemical formation of α-glycols

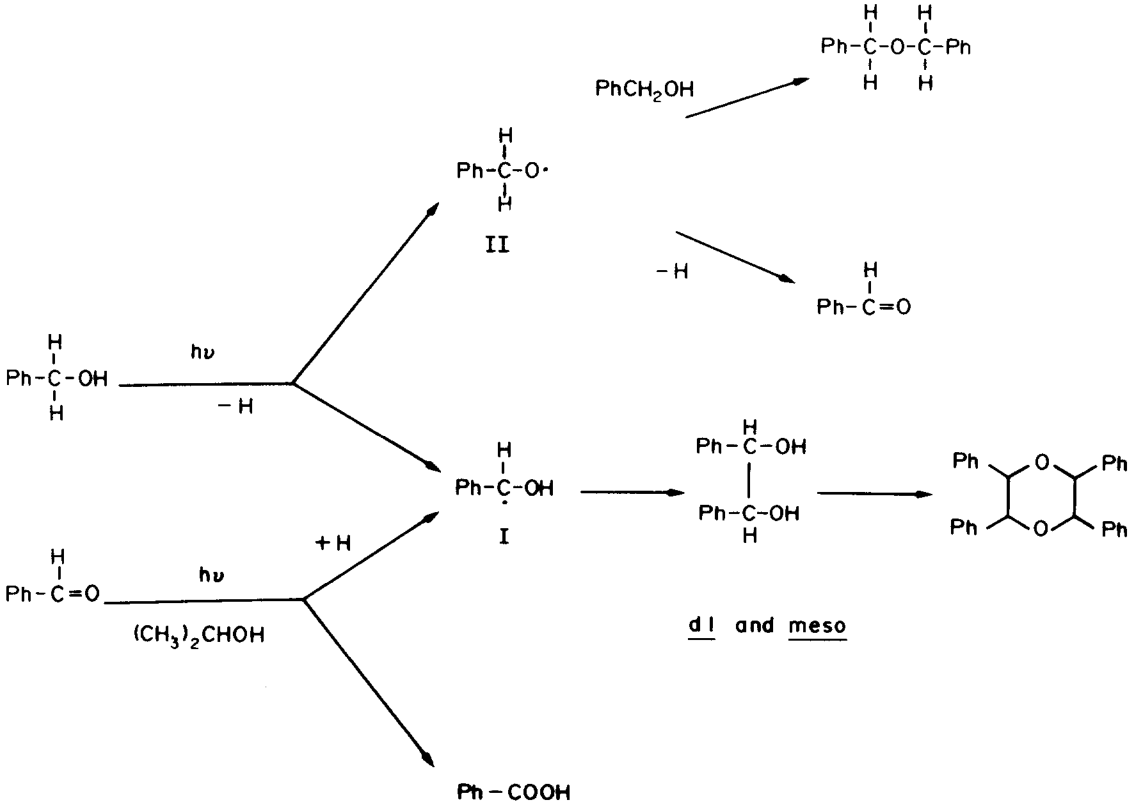
Comparison of photodehydrogenation of alcohols with the photoreduction of carbonyl compounds. As it is known α-glycols can be obtained by photoreduction of carbonyl compounds. So we believed that it should be interesting to compare the results obtained by irradiation of alcohols with those obtained from carbonyl compounds.[18,19] It was specially interesting to know if the stereochemistry of both photoreactions, measured through the *dl*/*meso* ratio, was the same. This comparative study was performed only with aromatic compounds (alcohols and aldehydes or ketones) because for the aliphatic carbonyl compounds the Norrish I and II reactions are very important.[20]

The fundamental difference between both reactions is the mechanism of formation of the hydroxyalkyl radical **1** (Scheme 1).

The products obtained in several irradiations, their yields and the values of the *dl* to *meso*-α-glycol ratio are indicated in Table 5.

The most interesting result was the difference observed in the value of those ratios. So, during the photodimerization of the alcohol the *dl*/*meso* value was always smaller than that obtained by photoreduction of the corresponding carbonyl compound.

Bimolecular reduction of ketones (and aldehydes) to pinacols in the presence of a suitable hydrogen donor has been known for over 80 years.[21] Moreover just in 1966



Scheme 1.

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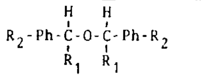
[a] The M.S. of the α-glycols will be reported in a future publication (R. Erra Balsells y A. R. Frasca, *AnalesAsoc. Quim. Argentina*).

[b] The irradiation of (2-MeO-phenyl) methanol with $NaBH_4$ (Table 1) shows that the radicals that are source of the carbonyl compounds and α-glycols are simultaneously formed.

Table 2. Properties of aromatic ethers

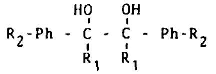


$R_2\text{-Ph-}\overset{H}{\underset{R_1}{C}}\text{-O-}\overset{H}{\underset{R_1}{C}}\text{-Ph-}R_2$

			m.p. or b.p.	GLC[a]	^{1}H-NMR[b]			
R_1	R_2	comp.N°		RRt	δ CH_3;CH_2 or OCH_3	δ $PhCH_2O$-	δ PhCH-O	δ aromatic protons
H	H	I	b.p.298°[4,5]	6.90	-	4.56(s)	-	7.34(s)
H	4-MeO	II	b.p.280°[6,7]	9.20	3.73(s)	4.45(s)	-	H_2;H_6;$H_{2'}$ and $H_{6'}$ 7.27(d, J 8.5 Hz) H_3;H_5;$H_{3'}$ and $H_{5'}$ 6.85(d, J 8.5 Hz)
Me	H	[c] III diast.A	b.p.282°[d,8]	10.20	1.36(d, J 6 Hz)	-	4.25(c, J 6 Hz)	7.33(s)
		[c] III diast.B	b.p.282°[d,8]	10.90	1.45(d, J 6 Hz)	-	4.53(c, J 6 Hz)	7.29(s)
Et	H	[c] IV diast.A	b.p.164°(14)[d,4]	10.90	0.79(t, J 5.5 Hz)	-	3.98(t, J 7 Hz)	7.30(s)
		[c] IV diast.B	b.p.164°(14)[d,4]	11.60	0.88(t, J 5.5 Hz) both CH_2 1.40-2.12(m)	-	4.32(t, J 7 Hz)	7.20(s)
Ph	H	V	m.p.109°[9]	14.70	-	-	5.39(s)	7.05-7.40(m)

a) the relative retention times (RRt) are given in min. using ethanol as internal standard.
b) ^{1}H-NMR spectra: solvent Cl_3CD, concentration 5%, δ values are given.
c) the ^{1}H-NMR spectrum was obtained from the diastereomers mixture.
d) b.p. of the mixture of diastereomers.

Table 3. Properties of symmetric aromatic α-glycols

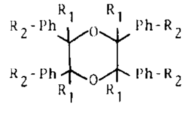


$R_2\text{-Ph - }\overset{HO}{\underset{R_1}{C}}\text{ - }\overset{OH}{\underset{R_1}{C}}\text{ - Ph-}R_2$

				m.p.[a]	GLC[b]	TLC[c]	^{1}H-NMR[d]			
R_1	R_2	comp.N°	config.		RRt	Rf	OCH_3 or CH_3	OH δ C-H	δ OH[e]	δ aromatic protons
H	H	VI	dl	120°[10,11]	7.07	0.32	-	4.68(s)	2.89(s)	7.19(s)
		VII	meso	132°[12]	8.11	0.26	-	4.83(s)	2.27(s)	7.26(s)
H	2-Cl	[f]	dl	-	6.99	0.28	-	5.29(s)	3.37(s)	7.14(s)
		VIII	meso	104°[g]	8.29	0.24	-	5.55(s)	2.77(s)	7.15(s)
H	2-MeO	IX	meso	152°[13]	8.13	0.19	3.68(s)	5.25(s)	2.68(s)	6.70-7.35(m)
H	4-MeO	X	meso	167°[14]	7.22	0.18	3.80(s)	4.75(s)	2.10(s)	H_2;H_6;$H_{2'}$ and $H_{6'}$ 7.20(d, J 8.5 Hz) H_3;H_5;$H_{3'}$ and $H_{5'}$ 6.85(d, J 8.5 Hz)
Me	H		dl	105°[15]		0.40	1.40(s)	-	2.58(s)	7.22(s)
		XI	meso	125°[16]	11.63	0.34	1.55(s)	-	2.45(s)	7.20(s)
Ph	H	XII		179°[17]	12.10	0.38		-	3.02(s)	7.20(s)

a) we only include those examples in which the separation and configuration assignment were performed.
b) the relative retention times (RRt) are given in min. using ethanol as internal standard.
c) silica-gel;benzene-EtOH 75:25.
d) ^{1}H-NMR spectra: Cl_3CD; concentration 5%; δ values are given.
e) in all examples this signal disappeared by adding D_2O.
f) the ^{1}H-NMR spectrum was obtained from the diastereomers mixture.
g) this value was checked with the m.p. of the authentic sample (see Experimental).

Table 4. Properties of 2,3,5,6-*tetra*-aryl-1,4-dioxanes



R_1	R_2	comp.N°	conform.	m.p.	GLC[a] RRt	TLC Rf	^{1}H-NMR[b] δ -CHO-	δ aromatic protons
H	H	XIII	b	81°	16.1	0.86	4.97(s)	7.31(s)
		XIII	a	81°	16.1	0.86	6.42(s)	7.17-7.77(m)
H	H	XIV	d	89°	15.5	0.84	5.51(s)	7.02(s)
		XIV	c	89°	15.5	0.84	6.20(s)	7.20-7.89(m)
H	2-Cl	XV	b	-	15.2	0.84	5.57(s)[c]	6.80-8.15(m)
		XV	a	-	15.2	0.84	6.75(s)[c]	6.80-8.15(m)
H	2-Cl	XVI	d	124°	14.8	0.82	6.10(s)	6.85-8.10(m)
		XVI	c	124°	14.8	0.82	6.49(s)	6.85-8.10(m)

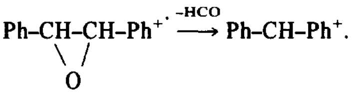
a) the relative retention times (RRt) are given in min. using ethanol as internal standard.
b) ^{1}H-NMR spectra: solvent Cl_3CD, concentration 5%, δ values are given.
c) the ^{1}H-NMR spectrum was obtained from the diastereomers mixture.

the first quantitative and stereochemical study was carried out. Stocker[22] irradiated acetophenone in neutral and acidic 2-propanol solution and he observed that the *dl* form slightly predominated over the *meso*. These studies were carried out with acetophenone-7-C^{14}, using isotope dilution techniques. Stocker explains his results considering that the formation of the H-bonding is necessary between the radicals that are going to couple to each other. This model could explain the *dl*/*meso* ratio obtained by photoreduction of carbonyl compounds but it is not able to explain the results obtained by photolysis of alcohols. This duality could be due to the fact that the radicals formed from alcohols are solvated[1] while those from carbonyl compounds are not. In the latter reaction the radicals approaching to form the *dl*- and *meso*-isomers have the same probability so the value of the ratio between them is approximately 1.

Origin and structure of 1,4-*dioxanes formed by irradiation of aromatic alcohols*

We already mentioned that during the irradiation of phenylmethanol two compounds were obtained as the principal reaction products: They were identified as 1,4-dioxanes (Tables 1, 4 and 9).

The gl chromatogram of the irradiation mixture showed two very important adjacent peaks. The isolation of the diastereomers was achieved by chromatography on alumina. The M.S. of both products (Table 9) were similar and only one of them (**XIII**) showed the molecular ion (*m*/*e* 392). This value agrees with the formula of *tetra*phenyl-1,4-dioxane ($C_{28}H_{24}O_2$). The base peak in both spectra at *m*/*e* 196 should be correlated to PhCHOCHPh ion. Likewise the peak at *m*/*e* 167 correlates to PhCHPh ion. The latter fragment could originate from the former through a typical rearrangement of phenylepoxides:[25]



$$\text{Ph-CH-CH-Ph}^{+\cdot}\xrightarrow{-\text{HCO}}\text{Ph-CH-Ph}^{+}.$$

The MS of the 1,4-dioxanes obtained by irradiation of (2-Cl-phenyl)-methanol confirm the above assignations (Table 9). The ^{1}H-NMR spectra of the *tetra*phenyl-1,4-dioxanes are represented in Figs. 1 and 2. They are very similar and show the peaks corresponding to Ph-CHO group (δ values between 4.90 and 6.50) and the aromatic

Table 5. Comparison of the products[a] obtained during irradiation of aromatic alcohols[b] with those obtained by photoreduction of the corresponding carbonyl compounds[c]

substrate	conv. %	ether %	α-glycol %	α-glycol dl/meso[d]	dioxane %	carbonyl prod. %
phenylmethanol	66	6	2	0.14	88	2
benzaldehyde	28	-	4	0.85	14	71
methyl phenylmethanol	31	60	10	-	-	3
acetophenone	20	-	78	0.96	-	-
2-Cl-phenylmethanol	53	-	11	0.26	38	4
2-Cl-benzaldehyde	12	-	73	1.17	-	1
4-MeO-phenylmethanol	50	77	6	-	-	1
4-MeO-benzaldehyde	10	-	48	0.92	-	1
diphenylmethanol	79	94	-	-	-	6
benzophenone	100	-	98	-	-	-

a) yields were calculated from converted substrate; for α-glycols and dioxanes correspond to the diastereomers mixture.
b) in all examples the irradiation time was 18 hr. When the phenylmethanol was irradiated during 6 hr the α-glycol yield in 39% and the 1,4-dioxanes yield in 9%.
c) see Experimental.
d) the ratios were determined from the reaction mixture by GLC analysis.

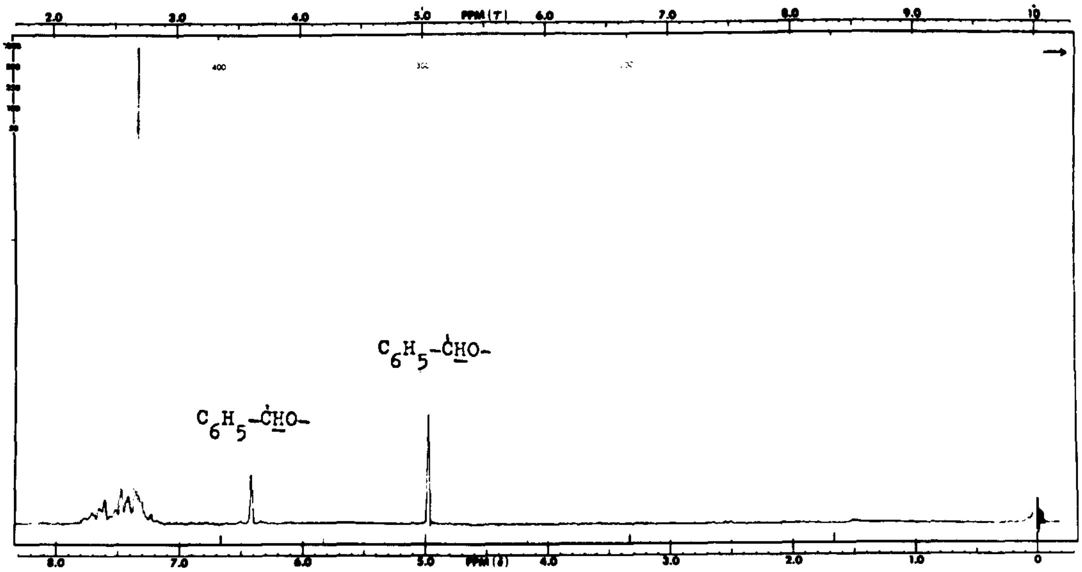


Fig. 1. ^{1}H-NMR spectrum of the *tetra*phenyl-1,4-dioxane **XIII**.

protons (about δ7). The value of the ratio between the area of methinic protons and also the absence of spin-spin coupling between them could discard those configurations where axial and equatorial H-atoms are simultaneously present. In the same spectra the ratio between the total area of methinic zone, as summation of all methinic peaks, and the area of aromatic zone is about 1:5. Hence, we suppose that each ^{1}H-NMR spectrum corresponds to one diastereomer. Each diastereomer exists as a mixture of two conformers so each singlet of the methinic zone correlates to a symmetric conformer whose H-atoms are equivalent.

The conformational analysis with molecular models shows that there are four conformations with all H-atoms equivalent: a and b for **XIII** and c and d for **XIV** (Schemes 2 and 3).

Considering that axial hydrogen atoms appear at smaller δ value than the equatorial one,[26] the ^{1}H-NMR spectra show that conformers with axial hydrogen atoms are predominant. In the conformers c and d the relative position of methinic H-atoms and aromatic groups are equivalent. The value $\Delta\delta_{c-d} = 0.69$ could be explained taking into account the different position of the H-atoms in respect to the ether linkage. A greater difference was observed on the other pair, a and b, because in this case besides of the mentioned effect the H-atoms of the conformer b are shielded by the vicinal aromatic groups and appear at lower δ values. Otherwise, in conformer a the aromatic groups have a rigid spatial position and there is not a shielding effect over methinic proton in fact there is a little deshielding effect. These two opposite effects on methinic H-atoms in the conformers a and b explain the greater $\Delta\delta_{a-b} = 1.45$ observed.

The above analysis suggests that ^{1}H-NMR spectrum of 1,4-dioxane **XIII** (Fig. 1) corresponds to the con-

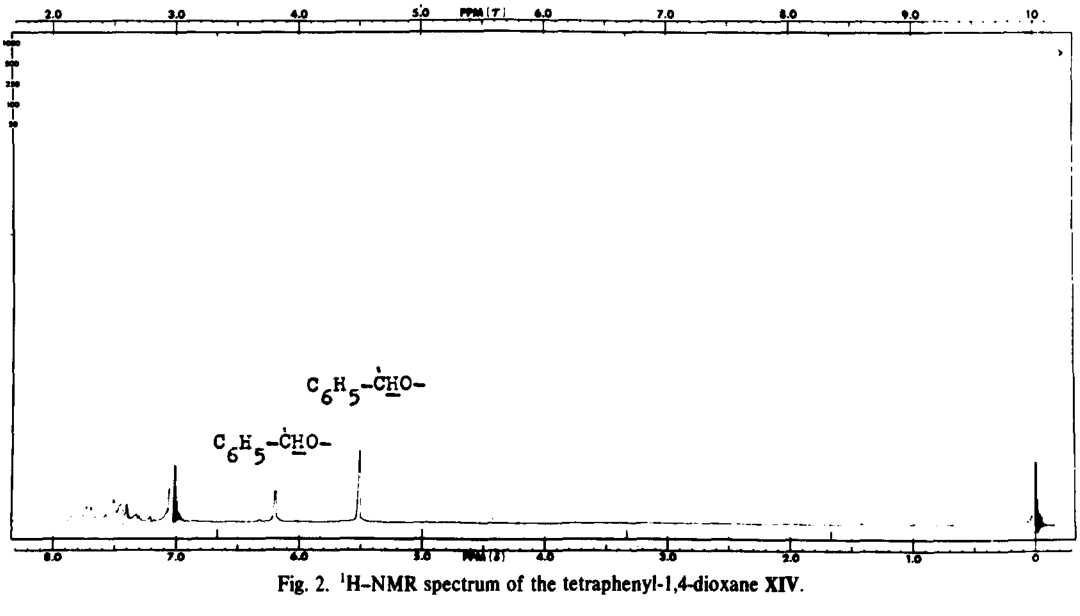
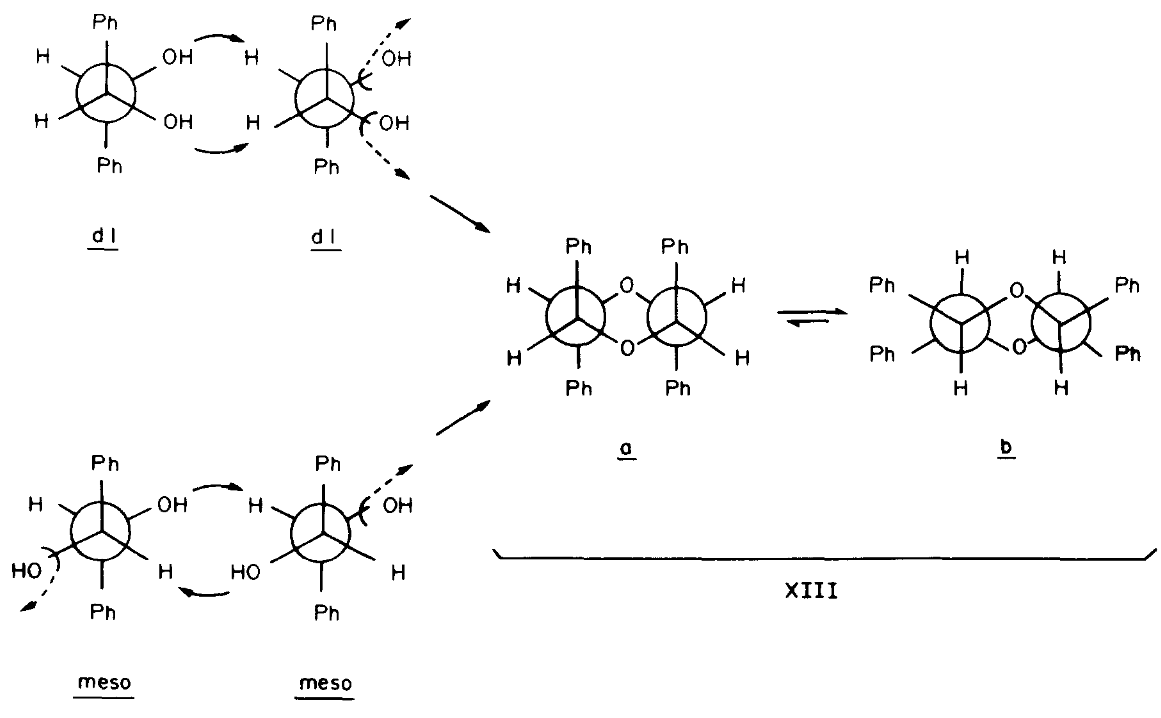


Fig. 2. ^{1}H-NMR spectrum of the tetraphenyl-1,4-dioxane **XIV**.



Scheme 2.

formers mixture a, b while that of the dioxane **XIV** (Fig. 2) corresponds to the c, d pair.

When the characterization of *tetra*phenyl-1,4-dioxanes was achieved, we studied the origin of such substances. It was already indicated that by irradiation of phenylmethanol we obtained: benzaldehyde, 1,4-dioxanes, *di*benzyl ether and 1,2-*di*phenyl-1,2-ethanediols. The dioxanes could be formed through two different pathways: (i) by oxidative dimerization of *di*benzyl ether or (ii) by dehydration of the *di*phenylethanediols because ethers and glycols are formed during the photoreaction.

The first pathway was discarded because no formation of 1,4-dioxanes was observed when we studied the photochemical and thermal stability of the corresponding ether.[c]

From the thermal and photochemical reaction of a mixture 1:1 of *dl* and *meso*-1,2-*di*phenyl-1,2-ethanediol (Experimental) similar mixtures of 1,4-dioxanes (**XIII** and **XIV**) were obtained. Hence we suppose that the 1,4-dioxane formation should be a thermal reaction. Moreover when the progress of the photolysis of phenylmethanol was monitored by glc we observed that at $t_1 = 6$ hr, the α-glycols predominated over 1,4-dioxanes while at $t_2 = 12$ hr the latter were the principal products. So, we assume that during this reaction first the α-glycols are formed (photoproducts) which are transformed into the dioxanes (thermal products) in a second step.

The isomer 1,4-dioxanes could be formed by a reaction of the diastereomer α-glycols, as follows: (i) *meso*-glycol + *meso*-glycol; (ii) *meso*-glycol + *dl*-glycol; (iii) *dl*-glycol + *dl*-glycol.

The comparison between the values of the ratio of α-glycol diastereomers (Table 5, *dl*/*meso* 0.14) and the ratio of 1,4-dioxanes (Table 1, **XIII**/**XIV** 0.27) shows that the predominant α-glycol, *meso* isomer, should be the precursor of both dioxanes because it is not probable that the minor glycol, *dl* isomer, participates in the formation of one of them. Besides, the thermal and photochemical stability of *meso*-α-glycol was studied and in fact, in both cases, the two dioxane isomers were obtained. On the other hand, only one isomer, **XIII**, was formed when the *dl*-glycol was submitted to similar treatments.

Taking into account that no interconversion between the *dl* and *meso*-α-glycols takes place (Experimental), it may be assumed that the *meso*-α-glycol is the precursor of the 1,4-dioxanes formed during the irradiation of phenylmethanol.

The above results could be explained with the following model of reaction: Two ether linkages are simultaneously formed during the reaction of two α-glycol molecules to yield 1,4-dioxane. This is supported by the non-formation of dimer products like PhCH(OH)PhCH–O–CHPhCH(OH)Ph. The two ether linkages could be formed if the two molecules of α-glycols approach each other as it is represented in Schemes 2 and 3. So, the dioxanes **XIII** and **XIV** are formed from *meso*-α-glycol in any of its two conformations. In the first case only one inversion occurs in each reactant molecule while in the second the two inversions occur simultaneously in the same molecule. According to this the reaction between two different *meso* conformers should not be possible.

The reaction of the *dl* isomer is similar. The H-bond present in the most stable *dl* conformer hinders the rotation around the C–C bond, so only one conformer can react which yields only one dioxane (**XIII**, Scheme 2).

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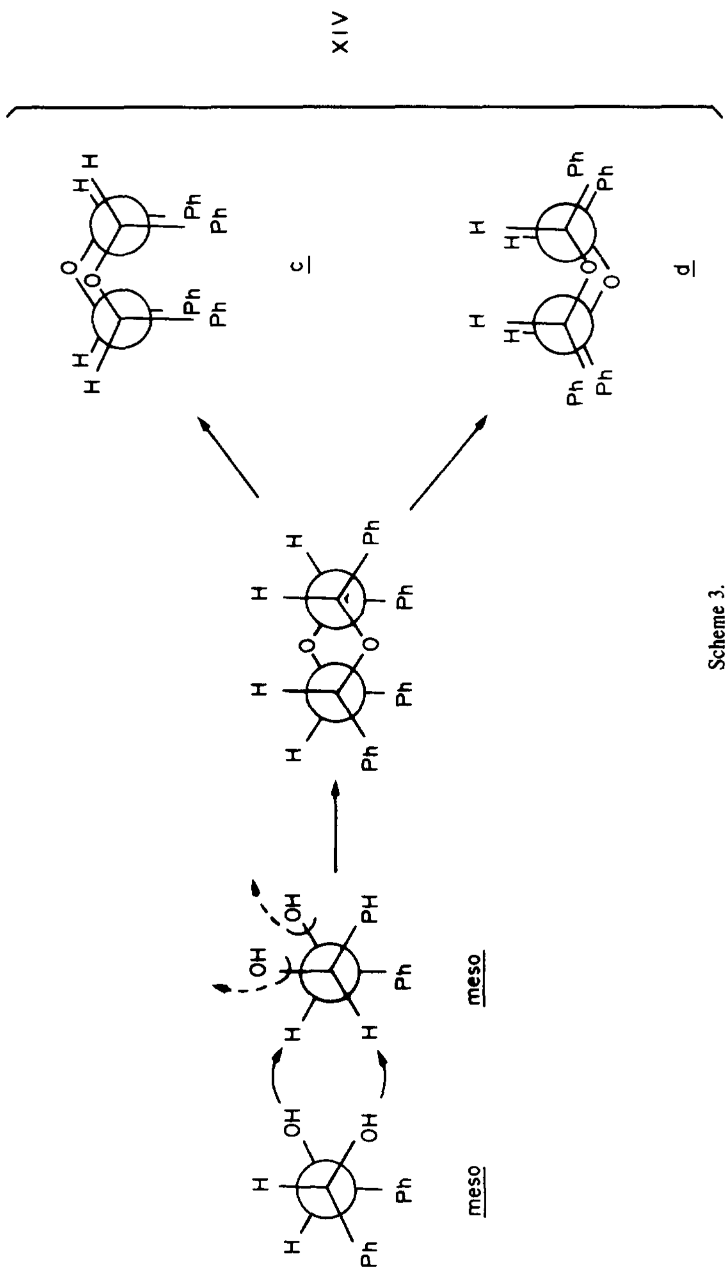
[c] The *di*benzyl ether (50 mg) dissolved in Cl_2CH_2 (50 ml): (i) was irradiated with a Hg high-pressure lamp; (ii) was heated in the dark at 60–70° for 17 hr.



Scheme 3.

Finally, we must point out that the value of the ratio of the 1,4-dioxanes obtained during the irradiation of phenylmethanol (**XIII/XIV** < 1) is different from that obtained by photodimerization of benzaldehyde (**XIII/XIV** ≅ 1). The difference could be explained by the formation of *dl*-glycol in a greater amount starting from benzaldehyde and because, as we already indicated, this isomer yields only **XIII**. During the irradiation of benzaldehyde a different 1,4-dioxane could be formed by dehydration of the system *dl*-glycol + *meso*-glycol. The ^{1}H-NMR spectra showed besides the peaks corresponding to **XIII** and **XIV** some additional small peaks that should be correlated to a dioxane structure, too. These minor products were not isolated.

Mechanism of the photochemical reaction of alcohols

The photochemical behavior of aliphatic and aromatic alcohols let us suppose that in both cases the electronic transition responsible of the photoreaction should be an n, σ^*.[27–36] This argument is supported by the kind of products obtained. So, due to the simplicity of its chromophore the photochemical formation of α-glycols is a general reaction of alcohols. The photodimerization with H-elimination has been described in only few cases using carboxylic acids,[37–38] aldehydes,[37] ketones[39,40] and ethers.[37,41–45]

In the alcohol group the O atom is simultaneously present in two different σ bonds, σ_{CO} and σ_{CH}. We suppose that the perturbation introduced by the n, σ^* transition will be located mainly at the σ_{CO} bond (H–C–O–H). This is a symmetric reaction model because two H-atoms are *alpha* to the excited bond. As in the photochemistry of carbonyl compounds,[20,48] the *alpha* homolytic fission of H-atoms in the alcohols is the most important non-emissive stabilization way, and two radicals, **I** and **II**, should be expected (Scheme 4). The preferential formation of one of them depends on certain aspects: bond stability, radical stability, effect of the substituents, etc.

It is interesting to mention that during the photolysis of alcohols we have not observed products derived from radical **III** (RR'HC·) like aliphatic and aromatic hydrocarbons. Hence we suppose that radical **III** is formed in a very low yield because light of shorter wavelength[30,31,49] is necessary for its formation.

We assume that the radicals **I** and **II**[d] are independently formed during the UV irradiation. ESR spectra described[50] for each radical support this assumption. However other authors[51,52] suppose that after the photon absorption only the radicals **II** are formed and they are then transformed into radicals **I** through a dark raction:

$$RR'CH\text{-}OH \xrightarrow{h\nu} \underset{\textbf{II}}{RR'CH\text{-}O\cdot} + H$$

$$\underset{\textbf{II}}{RR'CH\text{-}O\cdot} + RR'CH\text{-}OH \longrightarrow RR'CH\text{-}OH + \underset{\textbf{I}}{RR'\underset{\cdot}{C}\text{-}OH}$$

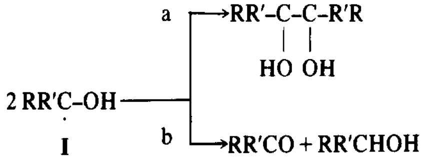
To test the conversion "radical **II** + alcohol→alcohol + radical **I**" under our experimental conditions, we studied the thermal stability of 1-butylhydroperoxide in 1-butanol solution (Table 6) because the alkyl-hydroperoxides are usually used as a source of radicals **II**:[54–58]

$$RR'CH\text{-}OOH \xrightarrow{\Delta} \underset{\textbf{II}}{RR'CH\text{-}O\cdot} + HO\cdot$$

During this experience we observed the formation of butyraldehyde but not of the corresponding α-glycol. This result let us assume that the radicals **II** are not transformed into the radicals **I** because it is known radicals **I** yield α-glycols.[e]

Also we studied the thermal and photochemical stability of 1-butylhydroperoxide and *di*phenylmethylhydroperoxide in phenylmethanol solution (Table 6); neither the first hydroperoxide nor the second yielded the α-glycol (1,2-*diphenyl*-1,2-*ethanediol*). It should be mentioned that the α-glycol is formed during the photolysis of phenylmethanol.

Although, it is well known[54–58] that the disproportionation is a typical reaction of radicals **II** (Table 7) Becker[47] and Sonntag[51] postulate the radical **I** as the precursor of α-glycols and carbonyl compounds:



$$\underset{\textbf{I}}{2\,RR'\underset{\cdot}{C}\text{-}OH} \begin{cases} \xrightarrow{a} RR'\text{-}\underset{HO}{C}\text{-}\underset{OH}{C}\text{-}R'R \\ \xrightarrow{b} RR'CO + RR'CHOH \end{cases}$$

Irradiations performed with several light sources support the independent formation of the radicals **I** and **II** (Table 8) because the products distribution was different. Thus, employing a Hg low pressure or a W lamp instead of the Hg high pressure lamp, the products derived from radicals **II** were the predominant.

The α-glycols are the usual products obtained during the photolysis of alcohols[60,61] and the photoreduction of carbonyl compounds[62,63] and they are formed by dimerization of radicals **I**. By irradiation of mixtures of two different alcohols we obtained three α-glycols formed by the three possible combinations of two different radicals **I**.[1]

The radical **I**, a secondary alkyl radical,[78,f] possesses a lifetime long enough that the glycol formation can be quenched. For this reason, we did not observe α-glycols (or 1,4-dioxanes) during the irradiation of the phenylmethanol-naphthalene mixture (molar ratio 4:1); otherwise, the products derived from radical **II** (ether and benzaldehyde) were obtained in good yields. In agreement with other authors[78] we think that radicals **II** have a very short lifetime, can hardly be quenched and

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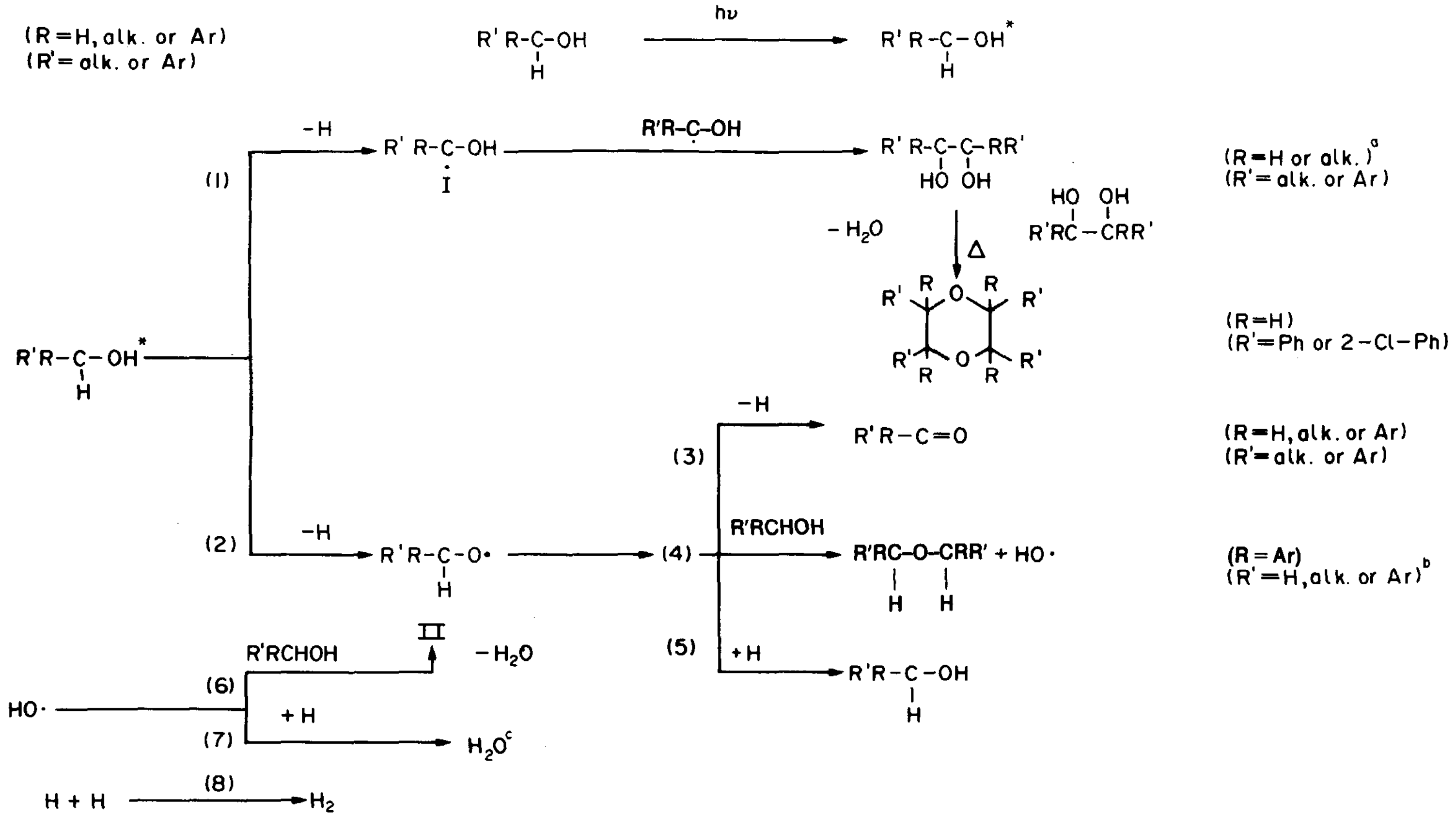
[d] The formation mechanism for radicals **II**:

$$\underset{\textbf{III}}{RR'\underset{\cdot}{C}H} \xrightarrow{O_2,h\nu} RR'CH\text{-}OO\cdot \xrightarrow{h\nu} \underset{\textbf{II}}{RR'CH\text{-}O.}$$

was discarded because when we irradiated *di*phenylmethanol in the absence of oxygen no change was observed. Also, the hydroperoxyradical seems to be not an intermediary of the reaction because the photolysis of 1-butanol[1] and the photolysis of 1-butylhydroperoxide (Table 7) gave different results.

[e] Takezaki[53] studied the kinetics of the decomposition of MeOH during the reaction with MeO·. He found ethyleneglycol as one of the reaction products. We think that these results are not opposite to the ours because the author worked in very different experimental conditions (high pressure, high temperature, vapour phase).

[f] The long life of secondary radicals is attributable to the βC–H bond present in the nodal plane of the orbital containing the unpaired electron.[78]



[a]The 1-phenyl-1-propanol gave no α-glycols.

[b]The 4-NO_2-*di*phenylmethanol and the (2-Cl-phenyl)- and (2-MeO-phenyl)methanol did not yield ethers.

[c]Ethers are not formed when this step is very important.

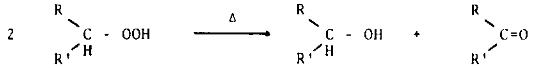
Scheme 4.

Table 6. Thermal stability of the hydroperoxide (R'RCH–OOH) alcohol mixtures[a]

mixture		method[b]	products obtained[c]			
hydroperoxide	alcohol		diphenylmethanol	benzophenone	1,1,1',1'-tetraphenyl methyl ether	other products
			%	%	%	%
	diphenylmethanol	A	-	-	600	-
		B	-	175	18	-
diphenylmethyl	phenylmethanol	A	23	52	-	phenol, 15;benzaldehyde 9
(R,R' = Ph)		B	24	52	-	phenol, 18;benzaldehyde 6
	1-butanol	A	22	50	-	phenol, 14;benzaldehyde 13
		B	22	50	-	phenol, 14;benzaldehyde 13
			1-butanol	butyraldehyde		
	diphenylmethanol	A	30	70	-	-
		B	28	66	3	-
1-butyl	phenylmethanol	B	25	68	-	1-butyl-phenylmethylperoxide 7[d]
(R = H)	1-butanol	A	-	60	-	-
(R' = Pr)		B	-	60	-	-
		C	-	69	-	1-butylperoxide 29[e]

a) *the mixtures were dissolved in Cl_2CH_2(10 ml) and the solns were heated in the dark at 60-70° for 18 hr.*
b) ratio hydroperoxide to alcohol (mol:mol); method A 1:10; method B 6.5:10; method C 9.1:10.
c) the reaction mixture was chromatographed on silica gel; each product was identified from their m.p.(or b.p.), Rf, RRt and IR. Yields were calculated from the hydroperoxide used. The yields of 175% for benzophenone and 600% for ether V showed that the reaction happened through a radical chain mechanism.
d) this compound was hydrolyzed using HCl soln, according to Abraham[58] and characterized by benzaldehyde and butyraldehyde formation (GLC and tlc).
e) the authentic sample was prepared according to Welch[59] technique. Viscous liquid, prickly odor, b.p. 80°(25 mm).

Table 7. Thermal and photochemical stability of hydroperoxides



$$2\ \mathrm{RR'CH{-}OOH} \xrightarrow{\Delta} \mathrm{RR'CH{-}OH} + \mathrm{RR'C{=}O}$$

hydroperoxide	method[a]	products obtained[b] alcohol %	carbonyl prod. %	other products %
diphenylmethyl[c]	A	20	42	phenol, 14;
(R,R' = Ph)				benzoic acid-benzaldehyde, 18
	B	42	58	-
1-butyl[d]	A	32	63	-
(R = H)	B	-	-	butanoic acid[e]
(R' = Pr)				

a) the hydroperoxide(100 mg) was dissolved in Cl_2CH_2(10 ml). (A) the soln was left in the dark at 60-70° for 18 hr; (B) the soln was irradiated in a manner similar to that used for aromatic alcohols.

b) the reaction mixture was chromatographed on silica gel column; each product was identified from their m.p.(or b.p.), Rf, RRt and IR. Yields were calculated from hydroperoxide used.

c) colorless needles from petroleum ether-benzene, m.p. 49-50°[54-56]

d) colorless liquid, b.p. 160°(23 mm)[57]

e) the reaction mixture was very complex. We only identified the butanoic acid by GLC analysis.

easily give unimolecular reactions (for example, disproportionation).

As shown in Scheme 4 the irradiation of aromatic alcohols led to the formation of the corresponding ethers. The photochemical origin of these products has been demonstrated because the ethers were not formed when the alcohols were heated in the dark at the same temperature reached during the photolysis of the alcohols. Hence, the steps 4 and 6 (Scheme 4) should constitute the most probable ether formation way.[g] To prove it we studied the thermal stability of some hydroperoxides. The most interesting result was obtained when we used the *di*phenylmethyl hydroperoxide-*di*phenylmethanol mixture (Table 6, Method *A*). The ether was the only product obtained and also it was observed the complete conversion of the alcohol. This result confirms the radical character of the mechanism of the ether formation (steps 4 and 6).

The simple initiator role of the hydroperoxides was shown during the thermal decomposition of the 1-butyl hydroperoxide-*di*phenylmethanol mixture (Table 6, Method *B*). Only one ether was obtained, V, together

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[g] Another mechanism could be represented as follows:

$$\underset{\mathrm{II}}{\mathrm{ArRCH{-}O\cdot}} + \underset{\mathrm{III}}{\mathrm{\cdot CHRAr}} \rightarrow \mathrm{ArRCH{-}O{-}CHRAr}$$

but we already indicated that the radical III is not formed in an appreciable amount. Taking into account that the arylmethane derivatives are sources of radicals III[64-67], we irradiated mixtures of phenylmethanol-phenylmethane and *di*phenylmethanol-*di*phenylmethane and no changes were noted in the products distribution respect to that obtained during the photolysis of each alcohol. These results show that the above *di*radical mechanism could be discarded.

Table 8. Irradiation of alcohols employing different light sources

alcohol	products	light sources Hg high p. %	Hg low p. %	W %
ethanol	acetic acid	8	93	95
	2,3-butanediol	78	-	-
1-butanol	butanoic acid	5	82	83
	4,5-octanediol	81	-	-
phenylmethanol	1,1'-diphenyl methyl ether	6	80	-
	2,3,5,6-tetraphenyl-1,4-dioxane	88	11	-
	benzaldehyde	2	3	60
	1,2-diphenyl-1,2-ethanediol	2	-	-
diphenylmethanol	1,1,1',1'-tetraphenyl methyl ether	93	94	-
	benzophenone	6	5	93

Yields were calculated from converted substrate.

Table 9. MS of the 2,3,5,6-*tetra*-aryl-1,4-dioxanes *m/e* (%)

assignment	dioxane			
	XIII	XIV	XV*	XVI
$M^{+\cdot}$	392(1)	-	528(1)	528(1)
$M-R_2PhCH_2$	301(2)	301(1)	-	-
$M-R_2PhCHO$	286(3)	286(2)	-	388(1)
$M-(PhCH_2)_2$	210(18);211(6)	210(17);211(4)	-	-
$M-(R_2PhCH)_2O$	196(100);197(17)	196(100);197(12)	264(46)262(73); 229(72)227(86); 194(40)	264(44)262(66); 229(27)227(84); 194(8)
$M-(R_2PhCH)_2O-CHO$	167(58)	167(40);168(12)	235(18); 200(28); 165(36)	235(14); 200(30); 165(5)
$M-(R_2PhCHO)_2$	180(3)	180(7);179(12)	248(1); 178(2)	248(3); 178(5)
$M-(R_2PhCHO)_2-H_2$	178(16)	178(14)	-	-
$M-(R_2PhCH)_3-HO$	105(22)	105(62);106(12)	139(34)	139(52)
$M-(R_2PhCH)_3-HO_2C$	77(15);63(6);51(6)	77(28);63(5);51(10)	111(60) 76(12);63(22);51(30)	111(14) 76(30);62(9);50(7)
$M-(R_2PhCH)_3O_2$	90(43);89(33)	90(21);89(26)	124(19) 89(100)	124(18) 89(100)

* the MS was obtained by GLC-MS from the diastereomers mixture.

with the usual thermal decomposition products of the 1-butyl hydroperoxide.[h]

By dehydrogenation of the radicals **II**, aldehydes and ketones[i] could be formed (Scheme 4). If no other acceptor is present, the radical **II** can accept hydrogen and yields the alcohol (Table 7). It is noteworthy that the authors who studied the photolysis of the alcohols have not proposed this simple thermal way as the formation mechanism of carbonyl compounds. Instead, they suggest several mechanisms: (i) from radicals **I**;[30,51,52] (ii) H_2 loos from the excited alcohol by a non-radical mechanism;[31,32,52,68–71] (iii) interaction between the radicals **I** and **II**[52] and (iv) interaction between the radicals **I** and **III**.[52]

We cannot discard the possibility that other mechanisms contribute to the formation of carbonyl compounds but our experience with hydroperoxides shows that there is no doubt about the very important participation of radicals **II** in this reaction.

To complete the analysis of Scheme 4, we must remember that *tetra*phenyl-1,4-dioxanes are formed by a thermal reaction from the α-glycols.

The only alicyclic alcohol studied showed an apparently different photoreactivity. During the irradiation of cyclohexanol, we obtained hexanoic acid, cyclohexyl hexanoate and cyclohexanone but no ether nor α-glycol.[1] Taking into account that cyclohexanone yields hexanoic acid[72] we considered that the keto compound could be the intermediary of this reaction. Moreover the irradiation of degassed cyclohexanol during different time intervals showed the same products distribution.

We assume that in the photolysis of cyclohexanol the radicals **I** and **II** are also formed but now the radical **I** is formed by an homolytic cleavage of the *alpha* C–C bond instead of the *alpha* C–H bond and this radical yields hexanoic acid and cyclohexyl hexanoate.

The postulated formation of radicals **I** has found further support on the mass spectrum described for cyclohexanol.[25] So, when deuterated-C_1-cyclohexanol was used, the M-2 ion was formed in low yield while the *alpha* cleavage of the C_1–C_2 bond was the most important step. Hence, the postulated photochemical behavior for the cyclohexanol is similar to the one already suggested for aliphatic acyclic alcohols (Scheme 4).

EXPERIMENTAL

The apparatus used for m.p.; IR; UV; ^{1}H-NMR; MS and GLC determinations have been described in Part I of this series.[1] GLC-MS spectra were recorded on a Hewlett-Packard GC/MS 5995A with FDD 9885M. Glc analysis were conducted using (i) a column 6 ft × 1.5 mm of 3% OV-17 on 80–100 mesh diatomite W for aromatic ethers and alcohols; (ii) a column 6 ft × 1.5 mm of 2% OV-1 on 60–80 mesh diatomite W for aromatic alcohols, aldehydes and ketones and *tetra*-aryl-1,4-dioxanes; (iii) a column 6 ft × 1.6 mm of 3% OV-101 on 60–80 mesh diatomite W for aromatic alcohols, aldehydes and ketones and *tetra*-aryl-1,4-dioxanes and (iv) a column 6 ft × 1.6 mm of 3% SE-30 on 60–80 mesh diatomite W for aromatic alcohols, aldehydes and ethers and *tetra*-aryl-1,4-dioxanes.

Compounds used in this work—Alcohols. The aromatic alcohols used were "Practical Grade reagents". They were redistilled and characterized from their b.p. and ^{1}H-NMR spectra. Glc analysis and IR spectra showed that the carbonyl compounds, as impurities, were absent.

1-Phenylethanol, 1-phenyl-1-propanol, *di*phenylmethanol, (2-MeO-phenyl)methanol and (4-MeO-phenyl)methanol were prepared from the corresponding carbonyl compounds by reduction with $NaBH_4$.

(2-Cl-*Phenyl*)*methanol* was prepared using a different method

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[h] Although we used the thermal decomposition of hydroperoxides as a model to interpret the photochemical formation of ethers, we must indicate the differences that exist between both reactions (thermal decomposition of *di*phenylmethyl hydroperoxide-*di*phenylmethanol mixture, and photolysis of *di*phenylmethanol). The thermal reaction between the hydroperoxide and the alcohol is a radical chain reaction and all the alcohol is converted into the ether. Otherwise, during the alcohol photolysis the ether is formed in good yield but some alcohol is recovered (34%). The different result could be explained taking into account that several possibilities to cut the radical chain exist in the irradiated solution (presence of H; formation of colored products, polymers and radical quenching).

[i] During some irradiations carboxylic acids and/or esters were obtained as normal products of the photo-oxidation of the alcohols.[1]

from that described in lit.[73] The 2-chlorotoluene was mono-brominated on *alpha* position through a photochemical reaction according to the method described[74] for 3-chlorotoluene. Further alkaline hydrolysis of the 2-chlorobenzyl bromide (NaOH 20%, during 4 hr) yielded the (2-Cl-phenyl)methanol. Colorless plates from benzene-EtOH. M.p. 70–71° (lit[73,75] 71°) MS *m/e* (%), 144(3); 142(9); 123(3); 121(34); 119(99); 117(100); 107(11); 105(3); 84(15); 82(23); 79(18); 78(3); 77(23); 59(5); 58(6); 51(7); 49(7); 47(24).

4-NO_2-*Diphenylmethanol* was prepared from the 4-nitrobenzophenone[76] by reduction with $NaBH_4$.

Carbonyl compounds. The aldehydes and ketones used in these experiences were "Practical Grade reagents" and the purification and characterization were realized in the usual manner.

Ethers. These compounds were purified and characterized as above.

α-Glycols. Several aromatic α-glycols were prepared by thermal reactions and were used as model compounds. The ^1H-NMR spectra are described in Table 3. *dl-1,2-Diphenyl-1,2-ethanediol*: this glycol was prepared from *trans*-stilbene according to the method described by Grignard.[12] The bromination of stilbene[10] followed by acetylation and hydrolysis[11] yields the *dl*-α-glycol. Colorless plates, m.p. 118–120° (lit[10–12] 118° and 120°). dl-2,3-*Diphenyl-2,3-butanediol*: This glycol was prepared from acetophenone and Mg amalgam according to the method described by Ramart-Lucas.[77] Colorless needles, m.p. 104–105° (lit[15,16] 105°). Finally four different *meso*-1,2-*di*phenyl-1,2-ethanediols were prepared from the corresponding benzaldehyde by reaction with Zn and glacial acetic acid.[12] meso-1,2-*Diphenyl-1,2-ethanediol*, colorless plates from benzene-ligroin, m.p. 131–132° (lit[12] 134°). meso-1,2-*Di*(2-MeO-*phenyl*)-1,2-*ethanediol*, colorless plates from benzene-EtOH, m.p. 152° (lit[13] 154°). meso-1,2-*Di*(4-MeO-*phenyl*)1,2-*ethanediol*, colorless plates from benzene-EtOH, m.p. 167° (lit[13,14] 167–168°). meso-1,2-*Di*(2-Cl-*phenyl*)-1,2-*ethanediol*, colorless plates from benzene-EtOH, m.p. 101–102° (Found: C, 59.29; H, 4.00; Cl, 25.29. $C_{14}H_{12}O_2Cl_2$ requires: C, 59.38; H, 4.27; Cl, 25.04%). Together with the *meso* isomer we obtained the *dl* form, dl-1,2-di(2-Cl-phenyl)-1,2-*ethanediol*, and was characterized by I.R. and ^1H-NMR spectra.

General method of irradiation of the aromatic alcohols

The aromatic alcohols (500 mg) were irradiated in Cl_2CH_2 solns (50 ml) with magnetic stirring, placed in quartz Erlenmeyer flasks (100 ml) fitted with a condenser. The light source was a Hg high pressure lamp[j] (Hanau-Quarzlampen G.m.b.H, TQ 150) which was placed 10 cm from the Erlenmeyer flasks. The progress of the reaction was followed by glc and tlc (silica gel, benzene-petroleum ether and benzene-EtOH). The spots on the tlc plates were developed with I_2. Irradiation time was 18 hr and the liquid reached a maximal temp of 60–70°.

The tlc analysis of the reaction mixture usually showed the presence of several products. Only the phenylmethanol gives all the above products mentioned which are ordered, according to decreasing R_f values as follows: 2,3,5,6-*tetra*phenyl-1,4-dioxane **XIII**; 2,3,5,6-*tetra*phenyl-1,4-dioxane **XIV**; *di*benzyl ether **I**; benzaldehyde; phenylmethanol; *dl*-α-glycol **VI** and *meso*-α-glycol **VII**. This sequence was the same in the other examples studied although the solvents polarity were different. In some examples we used two complementary tlc plates or columns of different polarities to observe all the products. Taking into account the example of the photolysis of the phenylmethanol, the reaction products are ordered, according to higher RRt values as follows: benzaldehyde: phenylmethanol; *di*benzyl ether **I**; *tetra*phenyl-1,4-dioxane **XIV**; *tetra*phenyl-1,4-dioxane **XIII**; *dl*-α-glycol **VI** and *meso*-α-glycol **VII**.

The ratios of the different diastereomers were calculated from the integrated chromatograms (Tables 1 and 5).

The reaction mixture was chromatographed on silica gel or alumina. Petroleum ether or mixtures of petroleum ether-benzene and benzene-EtOH were used as eluants. The purified products were characterized from their physical, spectroscopical and chromatographic properties (Table 2, 3, 4 and 9[k]). The conversion (%) of each alcohol and the yields (%) of each product are indicated in Table 1.

Moreover, to compare the results obtained during the irradiation of aromatic alcohols in Cl_2CH_2 solns with those obtained in the aliphatic series,[1] we irradiated some aromatic liquid alcohols (phenyl-methanol, 1-phenylethanol and 1-phenyl-1-propanol) without solvent. Similar results were obtained in both cases and also when the irradiations were realized in a degassed system.

Finally, we proved the photo-origin of the ethers and α-glycols indicated in Table 1 through the following experiences: The aromatic alcohol in Cl_2CH_2 soln was left in the dark at 60–70° for 15 hr. The glc and tlc analysis showed that neither the ethers nor the α-glycols were formed without the light source.

Irradiation of the aromatic carbonyl compounds

The aromatic aldehydes (or ketones) were dissolved in i-PrOH to which glacial acetic acid was added.[22] The solns were degassed with a fine stream of N_2 (30 min before and during the reaction) and were irradiated according to the General Method for 18 hr.

The residue obtained by evaporation of the solvent was chromatographed on silica gel or alumina as was already indicated.

The products (Table 5) were compared with those formed during the photolysis of the aromatic alcohols (Tables 3 and 4).

Thermal and photochemical stability of aromatic α-glycols

The 1,2-*di*aryl-1,2-ethanediols obtained during the irradiation of aromatic alcohols were used as substrates in thermal (**A**) and photochemical (**B**) experiences.

meso-1,2-*Diphenyl-1,2-ethanediol.* (**A**). The glycol (40 mg) was dissolved in phenylmethanol (10 ml) and was left in the dark at 60–70° for 15 hr. The non-converted *meso*-glycol (32 mg) and the dioxanes **XIII** and **XIV** (8 mg, yield 20%) were isolated from the mixture. The glc analysis and the ^1H-NMR spectra showed the predominance of the dioxane **XIV** over **XIII**. (**B**) The α-glycol (40 mg) dissolved in Cl_2CH_2 (10 ml) was irradiated with a Hg high-pressure lamp according to the General Method. The chromatography of the reaction mixture gave the following results: 1,4-Dioxanes **XIII** and **XIV** (3 mg, yield 7.5%) and *meso*-glycol (36 mg). In this example the glc analysis and the ^1H-NMR spectra showed that the dioxane **XIII** was the principal product.

dl-1,2-*Diphenyl-1,2-ethanediol.* (**A**). This reaction was conducted as in the above example. The *dl*-α-glycol was recovered almost unchanged while the glc analysis showed the presence of the dioxane **XIII** in very low yield. (**B**). The photolysis of the mentioned glycol yielded the dioxane **XIII** (3 mg) in 7.5% yield and 36 mg of the starting material were recovered without change.

Mixtures of dl- *and* meso-1,2-diphenyl-1,2-ethanediol. (**A**). The mixture formed by 20 mg of each isomer was dissolved in phenylmethanol (10 ml) and the reaction was performed as already described. The column chromatography of the reaction mixture allowed the isolation of 34 mg of the α-glycols mixture and 4 mg (yield 10%) of the dioxanes **XIII** and **XIV**. The ^1H-NMR spectra of the glycol mixture showed that the initial ratio *dl*/*meso* (1:1) was unaltered.

meso-1,2-*Di*(2-Cl-*phenyl*)-1,2-*ethanediol.* (**A**). The thermal treatment of this glycol gave in low yield (2 mg) the dioxanes **XV** and **XVI**, indicated in Table 4.

The irradiation of the other 1,2-*di*aryl-1,2-ethanediols showed only the formation of the aromatic alcohol and the carbonyl compounds and neither the interconversion of the isomers (*dl* to *meso* and *vice versa*) nor the formation of 1,4-dioxanes. Finally, when under our experimental conditions the thermal stability of these glycols were studied we did not observe any change.

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[j] The results obtained by using different light sources are in Table 8.

[k] The M. S. of the ethers and α-glycols obtained will be reported in a future publication (R. Erra Balsells y A. R. Frasca, *Anales Asoc. Quim. Argentina*).

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