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PHOTOCHEMICAL REACTION OF ALCOHOLS—I

IRRADIATION OF ALIPHATIC ALCOHOLS

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Abstract—The UV irradiation of aliphatic alcohols gave α-glycols as the principal products. The values of the *dl*-α-glycol to *meso*-α-glycol ratios obtained in each example were analyzed.

The stereochemical course of the formation of α-glycols, their conformations and configurations were established on the basis of ^{1}H NMR data.

During the study of the photochemical behaviour of some alkaloids and other nitrogen heterocycles in alcoholic solution, we found the reaction to be more complicated than we expected. This complication arose from the fact that the solvent reacted with the heterocycles. The formation of products, substrate-solvent, in certain irradiations in alcoholic solution, has been previously reported[1] but, although the aliphatic alcohols are usually used as solvents in organic photochemistry, their photochemical transformations have not been systematically studied. Previous studies[2–8] have not analysed certain important aspects of these transformations, and in some cases the results are contradictory. Hence, we undertook a detailed study of the photochemical behaviour of alcohols. Initially, we irradiated liquid ethanol contained in quartz Erlenmeyer flasks, employing a high pressure Hg lamp. The GLC analysis of the reaction mixture showed the formation of three products. This liquid mixture was distilled through a spinning band column under reduced pressure; the first fraction contained non-converted alcohol and the next acetic acid (Table 1). The glc analysis of the distillation residue showed two similar peaks (relative retention time, RR$_t$, 23.3 and 25.9 min) and its ^{1}H NMR spectrum corresponded to a mixture of two compounds, probably a pair of diastereomers. These compounds were separated by distillation and identified as *dl*-2,3-butanediol (I) and *meso*-2,3-butanediol (II) from their physical and spectroscopical properties (Table 2),† and from those of their *bis*-phenylurethans (Experimental).

Similar results were obtained when other aliphatic alcohols (1-PrOH, 1-BuOH, 1-pentanol and 3-Me-1-BuOH) were irradiated under the same conditions. In all cases both diastereomeric α-glycols were obtained, being the *meso*-glycol formed preferentially over the *dl*-glycol (Table 1). When 2-butanol was irradiated a sharp decrease in the *dl*- to *meso*-glycol ratio was observed and only the *meso*-glycol was formed during the irradiation of 2-Me-1-propanol. Only one α-glycol without asymmetric carbons, pinacol, was obtained from the irradiation of 2-propanol.

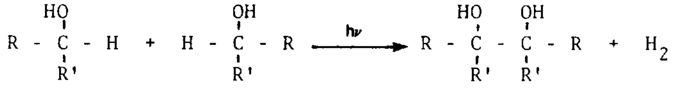
On the basis of these results, a mechanism is presented for the formation of the diastereomeric α-glycols. The reaction described herein may be used as a photochemical method to prepare α-glycols from alcohols (Scheme 1).

It is noteworthy that some aliphatic α-glycols may be obtained by the specific action of yeast on alcohols.[17–19] Also, α-glycols have been prepared by thermal,[20–22] enzimatic,[23–25] photochemical[26–30] and electrochemical[31,32] methods, from a variety of substrates.

The reaction of certain alcohols (EtOH, 1-PrOH, 1-BuOH and 2-Me-1-PrOH) presented no changes when we irradiated a degassed solution nor when the irradiation time was varied between 3 and 12 hr. Nevertheless, a very important change was observed when the alcohols were irradiated with W lamp or with a low pressure Hg lamp. Under these conditions, only ketones (or aldehydes) and carboxylic acids were isolated (Table 3).

The photochemistry of aliphatic alcohols has been studied by other authors, although their work is different from ours. Some authors[2–5] described as usual reaction products of the low molecular weight alcohols (MeOH, EtOH, 1- and 2-PrOH), CO, CO$_2$, CH$_4$ and carbonyl compounds. Glycols were not reported. In more recent publications Porter,[6] Yang[7] and Sonntag,[8] independently studied the analytical and quantitative aspects of this reaction and described the α-glycols formation. However, they did not mention the formation of the diastereomeric α-glycols mixture.

Only Leuschner[33] considered the formation of diastereomeric α-glycols, and separated them by crystallization. The solid product was always characterized as *meso*-α-glycol; from the filtrate he obtained a liquid product characterized as *dl*-α-glycol. The configuration of the α-glycols was assigned according to their reac-



$$\mathrm{R-\overset{HO}{\underset{R'}{C}}-H + H-\overset{OH}{\underset{R'}{C}}-R \xrightarrow{h\nu} R-\overset{HO}{\underset{R'}{C}}-\overset{OH}{\underset{R'}{C}}-R + H_2}$$

Scheme 1.

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†The mass spectra of the α-glycols obtained will be reported in a future publication.

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

alcohol	conv. %	carbonyl prod. %	α-glycol %	dl/meso[b]
ethanol	12	8[c]	78	0.81
1-propanol	14	8	78	0.61
2-propanol	17	12	71	-
1-butanol	47	5[c]	81	0.66
2-Me-1-propanol	30	3	90	0
2-butanol	22	5	82	0.16
1-pentanol	21	5	86	0.95
3-Me-1-butanol	38	-	74	0.63

a - yields were calculated from converted substrate; for α-glycols are expresed as a mixture of both diastereomers.
b - the ratios were determined from the mixture of the reaction by GLC analysis.
c - these compounds were identified as acetic and butanoic acid respectively

tivity towards HIO_4. In our opinion (see "Determination of the configuration of α-glycols") this method can not be used sistematically on aliphatic acyclic alcohols like Leuschner did.

We irradiated a cyclic alcohol, cyclohexanol, obtaining cyclohexanone hexanoic acid and cyclohexyl hexanoate (Experimental). The same photoreaction was observed when the liquid was degassed with a fine stream of nitrogen gas or when the irradiation time was modified (7, 17 and 72 hr).

These results indicate that α-glycols are not be formed during UV irradiation of cyclohexanol.

$$C_6H_{11}OH \xrightarrow{h\nu} C_6H_{10}O + CH_3(CH_2)_4COOH + CH_3(CH_2)_4COOC_6H_{11}.$$

The last result differs substantially from the one obtained with acyclic alcohols. Moreover, both photochemical reactions follow the same mechanism for radical formation, hence in acyclic alcohols a homolytic cleavage of the *alfa* C-H bond takes place, while in cyclohexanol the homolytic cleavage occurs at the *alfa* C–C bond (see Part II of this series).

It is noteworthy that cyclohexanol was irradiated by Leuschner[33] who curiously reported two diastereomeric α-glycols and following his usual methodology, characterized the liquid product as the *dl* and the solid product as the *meso* isomer.

Irradiation of mixtures of alcohols

Taking into account the above observations and other reported results,[2–5] we postulate that α-glycols are formed during the irradiation of alcohols by a radical mechanism. Hence if a mixture of two alcohols is irradiated symmetric and asymmetric α-glycols and carbonyl compounds should be simultaneously obtained. By the same reason the ratio between the asymmetric and symmetric glycols formed depends on the alcohols ratio in the original mixture. Our results (Table 4) confirm this idea. The choice of the mixture of alcohols to be irradiated was carefully made, because the photoreactions were followed by glc analysis and the RR_t of the α-glycols formed must be different. Always, we observed that the RR_t values of the asymmetric glycols were in between the RR_t values of the symmetric glycols (Fig. 1).

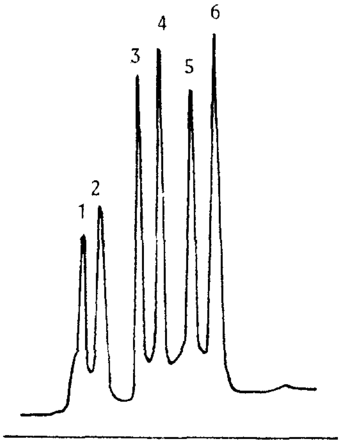

Fig. 1. Chromatogram of the products obtained from the irradiation of ethanol-1-butanol mixture; **1** *dl*-2,3-butanediol; **2** *meso*-2,3-butanediol; **3** and **4** diastereomers of the asymmetric α-glycol; **5** *dl*-4,5-octanediol and **6** *meso*-4,5-octanediol.

The mixtures were irradiated according to the general method (Experimental) and the products were characterized from their physical and spectroscopical properties (Tables 4 and 5). The asymmetric structure of the glycols obtained was clearly observed in their ^1H NMR (Fig. 4) and MS† because these spectra were equivalent to the one obtained by addition (or superposition) of the spectra corresponding to each symmetric α-glycol.

Determination of the configuration of α-glycols

To study the oxidative dimerization of alcohols to pinacols under the UV radiation and the formation of diastereomeric α-glycols we re-examined different methods usually used for determination of α-glycols configurations. Hence, we analyzed the utility of (i) the oxidation of α-glycols with HIO_4; (ii) the retention time values in glc analysis and (iii) ^1H NMR spectra.

Leuschner[33] used the first method for this purpose. He mentioned that in acyclic aliphatic alcohols the reaction of *meso*-glycols with HIO_4 was completed in a few

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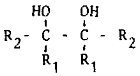
†The mass spectra of the α-glycols obtained will be reported in a future publication.

Table 2. Properties of the symmetric α-glycols

 $R_2\text{-}\overset{HO}{\underset{R_1}{C}}\text{-}\overset{OH}{\underset{R_1}{C}}\text{-}R_2$				m.p. or b.p.[a]	GLC[b]	^{1}H-NMR[c]				
R_1	R_2	comp.N°	config.		RR$_t$	$\delta\ \overset{OH}{C}$-H	δ OH[d]	δ CH$_2$-	δ CH$_3$-COH	δ CH$_3$-
H	Me	I	dl	b.p.92°(25)[9]	23.3	3.53(m,J 6 and 4Hz)	3.38(s)	-	1.16(d,J 6Hz)	-
		II	meso	b.p.100°(27)[9]	25.9	3.80(m,J 6 and 4Hz)	2.98(s)	-	1.13(d,J 6Hz)	-
H	Et	III	dl	b.p.82°(25)[10]	23.7	3.34(m)	2.95(s)	1.48(m)	-	0.96(t,J 6.5Hz)
		IV	meso	m.p.89°[10]	26.7	3.55(t,J 6Hz)	2.53(s)	1.45(c,J 6Hz)	-	0.99(t,J 6Hz)
Me	Me	V		b.p.172°(760)[11]	21.9	-	2.05(s)	-	1.22(s)	-
H	Pr	VI	dl	b.p.85°(25)[12-14]	26.0	3.40(m)	2.68(s)	1.44(m)	-	0.99(m)
		VII	meso	m.p.112°[12-14]	29.3	3.56(m)	2.25(s)	1.41(m)	-	0.94(m)
H	i-Pr	VIII	meso	m.p.154°[15]	37.8	3.45(m)	1.58(s)	1.80-2.10(m)[e]	-	0.94(d,J 6.5Hz)[f] 0.98(d,J 6.5Hz)[f]
Me	Et	g	dl		24.8	-	2.83(s)	1.49(c,J 7Hz)	1.13(s)	1.00(c,J 7Hz)
		IX	meso	b.p.82°(25)	27.8	-	2.80(s)	1.50(c,J 7Hz)	1.12(s)	1.05(c,J 7Hz)
H	n-Bu	X	meso	m.p.138°[16]	43.7	3.61(m)	2.23(s)	1.40(m)	-	0.94(m)
H	i-Bu	g	dl		28.9	3.45(m)	2.60(s)	1.18-1.45(m)	1.50-2-00(m)[e]	1.05(m)
		XI	meso	m.p.90°	31.9	3.74(m)	2.15(s)	1.20-1.50(m)	1.55-2.00(m)[e]	0.93 and 0.98[f] (d,J 6Hz)

a- we only include those examples in which the separation and configuration assignment were performed. Distillation pressures, given in parentheses, are in units of mm Hg.
b- the relative retention times (RR$_t$) are given in min. using ethanol as internal standard.
c- ^{1}H-NMR spectra: solvent CL$_3$CD; concentration 5%; δ values are given.
d- in all examples this signal disappeared by adding D$_2$O.
e- this signal corresponds to the methinic group of the α-glycol.
f- the non equivalent geminals Me groups are responsable of these signals.
g- the ^{1}H-NMR spectrum was obtained from the diastereomers mixture.

Table 3. 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	-	-

minutes while no reaction was observed, after several days, for *dl*-glycols. These results are opposite to those of Criegee,[34] Price[35] *et al.* reported.[36] Hence, we repeated some reactions with α-glycols of well-known configuration (Table 2). Our results (Experimental) showed that the oxidation with HIO_4 could not be used for the assignment of configuration of acyclic α-glycols unless these reactions were monitored in a very careful kinetic study. In this case the *dl*-isomer reaction should be faster.

The results mentioned above indicate that the stereochemical assignments carried out by Leuschner may be incorrect.

All the examples studied showed that the RR_t of *dl*-glycol was always smaller than that of the corresponding to the *meso*-glycol (Table 2); so the glc analysis is useful for the assignment of the α-glycol configuration, as a relative method. Hence a diastereomeric α-glycol mixture or one of them with assigned configuration are needed to be used as reference compound.

^1H NMR spectroscopy was the most useful technique for this purpose.† From the spectra we could usually decide whether we were dealing with one diastereomeric compound or a diastereomeric mixture, and determine the ratio between the diastereomers and their configurations. Employing pure diastereomers we were able to correlate the ^1H NMR spectrum to an individual conformation or a mixture of them.

The spectroscopical data useful for this purpose are: (a) position (δ values) and shape of the methinic signal (**H**-C-OH) and (b) position and shape of the signal for the other substituents of the carbinolic carbon (**RR**'C-OH).

Also the HO group appears at different δ values in the *dl*- and *meso* series,[40] but the ^1H NMR spectra must be done on pure diastereomers because no difference could be observed on a mixture of diastereomers.

The δ values of the carbinolic and hydroxylic protons and the other signals of *dl*- and *meso*-glycols are listed in Table 2. To explain these results we analyzed the different conformations that could be adopted by the *meso*-glycol (*a*, *b*, *c*) and the *dl*-glycol (*d*, *e*, *f*) (Scheme 2).

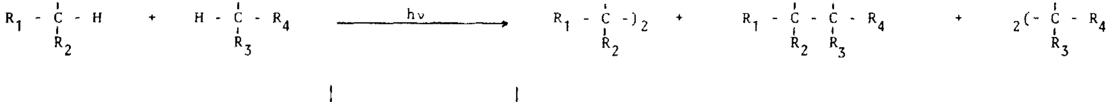
The preferred conformations for each isomers are those with bulky groups *anti* (*meso a* and *dl d*). Hence, the carbinolic proton of *meso a* form appears downfield from the corresponding one to *dl d* form by the influence of the *gauche* OH group in *d* form. A similar analysis explains the position of the protons of other carbinolic substituents (**R**-CH-OH) although with a smaller effect, and the absorption of the hydroxylic proton of the *dl* (*d*) glycol at higher chemical shift than the hydroxylic proton of the *meso* (*a*) glycol.

We also observed that the ^1H NMR spectra of *dl* glycol were always more complex than the corresponding spectra of the *meso* forms (an example is showed in Figs. 2 and 3). This result may be explained if we assume that the *dl*-glycols exist in two non-convertible conformations (*d* and *e*). Moreover the *dl* forms must exist to a considerable extent in the *d* conformation which explain the most intense signals while the *e* conformations explain the smaller signals with similar chemical shift values (CH-OH and CH_2CHOH, Fig. 3).

It is noteworthy that the methinic proton of the *e* conformation absorbs at a similar δ value as the same proton in the *meso a* form.

The presence of only one conformation for *meso* glycols and two conformations for *dl* glycols can be related with the mechanism of formation of α-glycols as we shall discuss below.

Table 4. Products obtained by UV irradiation of aliphatic alcohol mixtures (yield[a]%)



$$R_1-\underset{R_2}{\overset{HO}{C}}-H + H-\underset{R_3}{\overset{OH}{C}}-R_4 \xrightarrow{h\nu} R_1-\underset{R_2}{\overset{HO}{C}}-)_2 + R_1-\underset{R_2}{\overset{HO}{C}}-\underset{R_3}{\overset{OH}{C}}-R_4 + {}_2(-\underset{R_3}{\overset{OH}{C}}-R_4$$

R_1	R_2	R_3	R_4	method	conv. %	comp. N°	%	%	diast.ratio[b]	comp. N°	%
H	Me	H	Pr	A	18	I+II	10	75[c]	0.95	VI+VII	15
H	Me	H	i-Pr	A	21	I+II	30	60[c]	0.49	VIII	10
Me	Me	H	Et	A	20	V	33	54	-	III+IV	13
Me	Me	H	Et	B	20	V	12	44	-	III+IV	43
Me	Me	H	i-Pr	A	20	V	32	56	-	VIII	11
Me	Me	H	i-Pr	B	20	V	15	62	-	VIII	23

a- Method A: molar ratio 1:1; Method B: molar ratio 3:7. Yields were calculated from the converted materials.
b- these values correspond at the diastereomers ratio SR(or RS)/SS(or RR), and were determined from the reaction mixture by GLC analysis.
c- as a mixture of both diastereomers.

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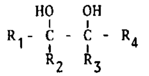
†After our first observations we found a report of Wiemann[39] that explains the ^1H NMR spectra of some α-glycols using only the preferred conformation of each diastereomer.

Table 5. Properties of the asymmetric α-glycols.

 $R_1-\overset{HO}{\underset{R_2}{C}}-\overset{OH}{\underset{R_3}{C}}-R_4$					m.p. or b.p.[a]	GLC[b]	^{1}H-NMR[c]				
R_1	R_2	R_3	R_4	comp.N°		RR_t	$\delta\ \overset{OH}{C}-\underline{H}$	$\delta\ O\underline{H}$[d]	$\delta\ C\underline{H}_2-$	$\delta\ (CH_3)_2C\underline{H}-$	$\delta\ C\underline{H}_3-$
H	Me	H	Pr	e	b.p.84°(25)	26	3.20-4.00(m)	3.60(s)	1.42(m)	-	1.12(d,J 6.5Hz)
						29					1.15(d,J 6.5Hz)
											0.95(t,J 6.5Hz)
H	Me	H	i-Pr		b.p.90°(35)	30	3.50-4.00(m)	2.68(s)	-	1.38-2.03(m)	0.79-1.38(m)
							3.00-3.30(m)				
				XIV	b.p.70°(23)	33.4	3.50-4.00(m)	2.77(s)	-	1.46-2.03(m)	0.78-1.39(m)
							3.15-3.45(m)				
Me	Me	H	Et	XV	b.p.119°(80)[37]	22.5	3.18-3.50(m)	2.53(s)	1.20-1.60(m)	-	1.22(s); 1.26(s)
											1.03(t,J 6.5Hz)[f]
											1.08(t,J 6.5Hz)[f]
Me	Me	H	i-Pr	XVI	m.p.58[g,38]	27.8	3.22(d,J 3.5Hz)	2.33(s)	-	1.65-2.15(m)	1.21(s); 1.26(s)
											0.96(d,J 6.5Hz)
											1.01(d,J 6.5Hz)

a- we only include those examples in which the separation and configuration assignment were performed. Distillation pressures, given in parentheses, are in units of mm Hg.

b- the relative retention times (RR_t) are given in min. using ethanol as internal standard. The RR_t of RS(or SR) isomer is always smaller than that of the RR(or SS) isomer.

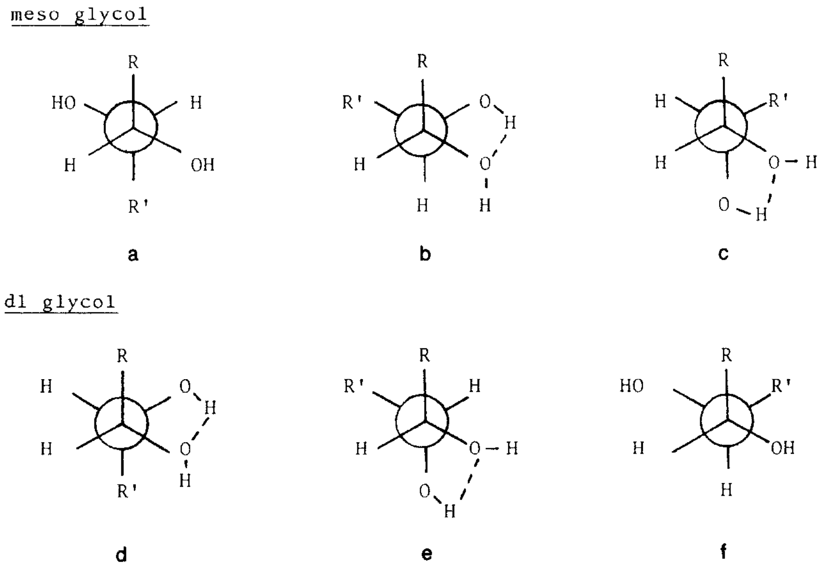
c- ^{1}H-NMR spectra: solvent Cl_3CD; concentration 5%; δ values are given.

d- in all examples this signal desappeared by adding D_2O.

e- we used the diastereomers mixture. In the spectrum the signal of Me groups at δ 1.12 and 1.15 correlate to the Me groups of the 2,3-butanediol isomers (meso δ 1.13 and dl δ 1.16).

f- the two triplets correspond to a mixture of conformers.

g- it was obtained by recrystallization (benzene-EtOH) from the fraction of b.p.97°(35).



Scheme 2.

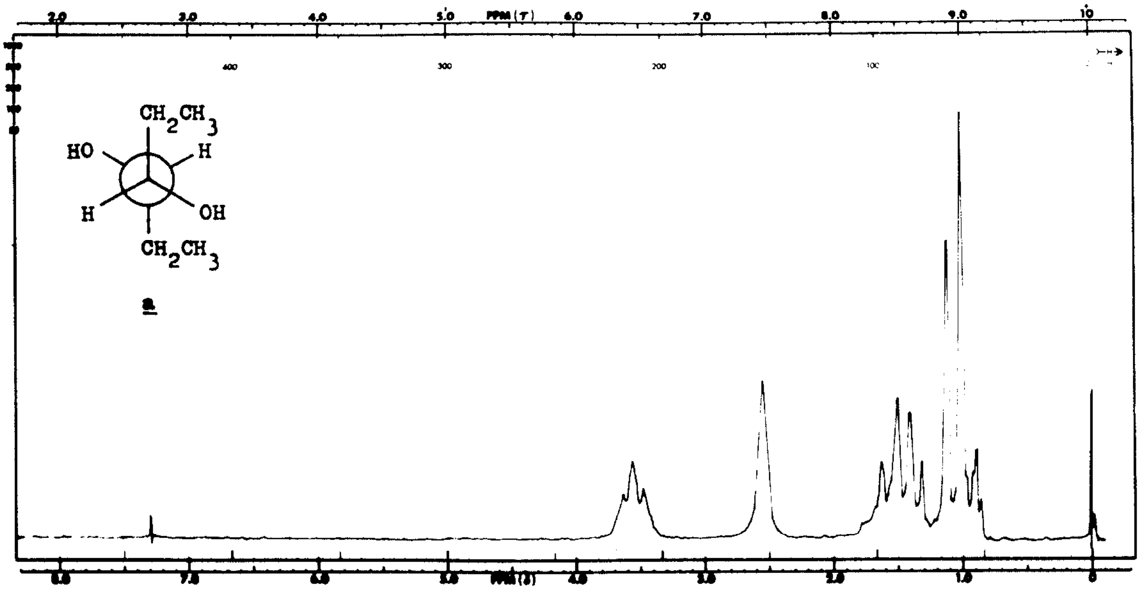
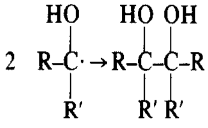


Fig. 2. ^{1}H NMR spectrum of the *meso*-3,4-hexanediol (IV).

Stereochemistry of the formation of α-glycols

In agreement with other authors[41] we believe that α-glycols are formed by the reaction of two hydroxymethyl radicals:†



$$2\ \mathrm{R{-}\overset{\displaystyle HO}{\underset{\displaystyle R'}{C}}\cdot \rightarrow R{-}\overset{\displaystyle HO}{\underset{\displaystyle R'}{C}}{-}\overset{\displaystyle OH}{\underset{\displaystyle R'}{C}}{-}R}$$

In the first examples studied we observed the formation of both diastereomers with the *meso* form predominating over the *dl* form. This difference increased in other examples studied and finally in a case the *meso-α*-glycol was the only glycol observed (2-Me-1-PrOH). The results (Table 1) showed that this was not a statistical radical reaction and that a directing factor should exist. Moreover the ratio between the diastereomers should be only related to their formation mechanism, because no changes were observed when we studied separately the thermal and photochemical stability of the *dl* and *meso-α*-glycols.

The hydroxymethyl radicals formed during the irradiation are pyramidal (sp^3 hibridization)‡ and rapidly transform to their mirror image by a low energy process. If the coupling between these radicals is at random both diastereomers should be formed in a similar proportion,

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†See Part II of this series.

‡Walsh[42] studied the electronic orbitals shapes and spectra of tetra-atomic hydride molecules AH$_3$. In their ground state AH$_3$ molecules containing not more than 6 valency electrons should be planar (sp^2) and molecules containing 7 or 8 electrons should be pyramidal (sp^3).

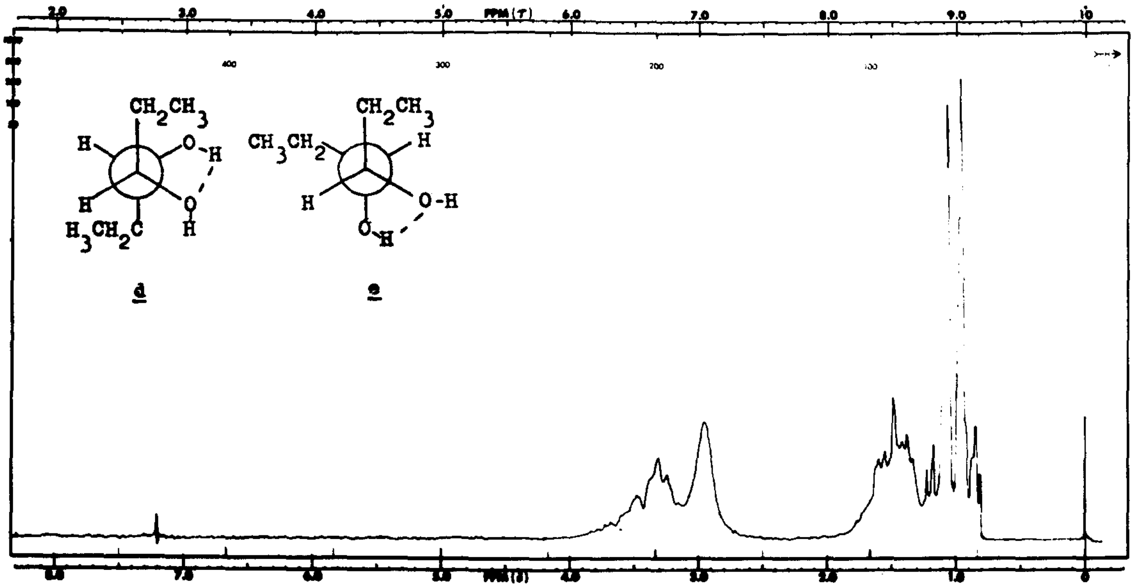


Fig. 3. ^{1}H NMR spectrum of the *dl*-3,4-hexanediol (III).

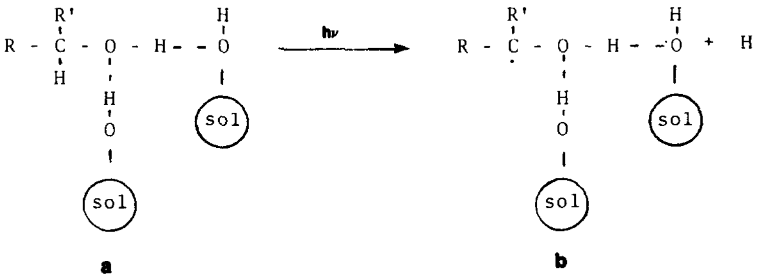
while if the steric repulsions[43] or the hydrogen bonding between the pair of radicals appear before their coupling[44,45] some preference in *dl* formation should be expected. Moreover, our results were different and also were highly stereoselective. So we present a mechanism to explain the stereochemistry of this reaction. Under our experimental conditions the presence of intramolecular H-bonding of the alcohol is easily accepted (Scheme 3, *a*). When these alcohols are irradiated the H-bonds are not affected and solvated free radicals are formed (Scheme 3, *b*).

Now, in these radicals the bulky group is the solvated hydroxyl group. This is the determinating factor of the reaction stereochemistry because the approximation of two radicals should be done with the bulky groups *anti*. So, to form the *meso* glycol they must approach according to the *a* form and for the *dl* glycol according to the *f* form (Scheme 4).

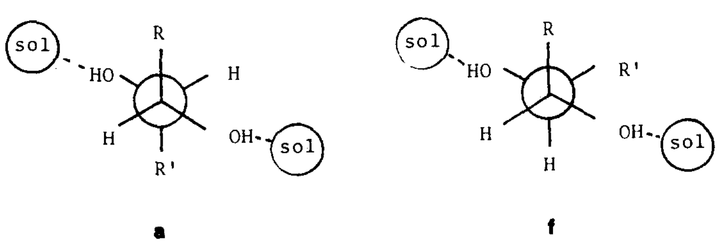
No other approximation forms are important because the bulky groups in them are *gauche* (Scheme 2).

On the other hand, in the *a* conformer only the R,HO(sol) interaction is important while in the *f* conformer an R,R interaction is also present. Hence, if R is a bulky group the ratio *dl*/*meso* should be smaller (Table 1). The R,R interaction increases from methyl to ethyl group, but no important changes were observed with longer substituent groups. This interaction is greatest when there are ramifications close to the carbinolic carbon (2-Me-1-PrOH). Also, the R,R interaction is very important when the carbinolic carbon is a secondary one (RR'C–OH, R and R' alkyl) (2-BuOH).

The conformations *a* and *f* are present in the irradi-



Scheme 3.



Scheme 4.

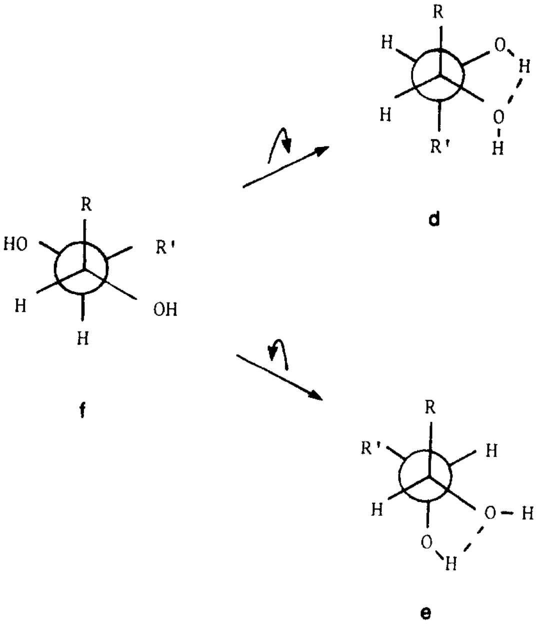
ated solution and when the α-glycols are isolated from the non-converted alcohol they can transform into more stable conformers. For the *meso* form the approaching and the most stable conformation (*a*) are coincident, while for the *dl* form the *f* conformation is not the most stable, so when the solvent is out the *f* form will transform to *d* or *e* forms (Scheme 5).

It is noteworthy that we have observed agreement between the proposed model for α-glycols formation and ^{1}H NMR spectra of symmetric α-glycols. This model is better understood when the α-glycol formed is asymmetric ($R \neq R'$). So, the ^{1}H NMR spectrum of the glycol obtained from the ethanol-2-Me-1-propanol mixture showed the presence of two asymmetric diastereomers in a 0.49 ratio (Table 4).

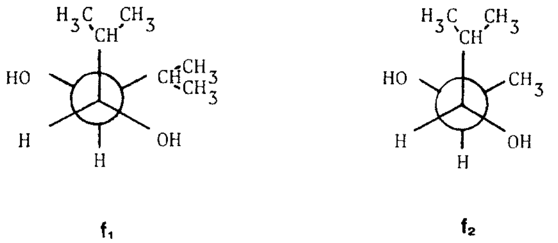
Taking into account the above model these radicals approach as *a* and *f* (R = Me and R′ = *i* − Pr). In the *a* form, with the bulky groups *anti* to each other, there are no important steric interactions while in the *f* form these interactions require a special analysis. In Scheme 6 are shown the approximation forms *f* of the radicals when pure 2-Me-1-propanol (f_1) and ethanol-2-Me-1-propanol mixture (f_2) were separately irradiated. In the asymmetric glycol (f_2) the minor steric interaction allows the C–C bond formation. Hence SR (or RS) α-glycol is obtained while for the symmetric glycol (f_1) the equivalent form (*dl* isomer) is not observed.

An interesting result was observed when an ethanol-1-butanol mixture was irradiated because not only two asymmetric diastereomers were obtained but also the ratio between them (Table 4, 0.95) was greater than the ratio obtained between *dl* and *meso*-4,5-octanediol (Table 1, 0.66). These examples are analyzed in Scheme 7.

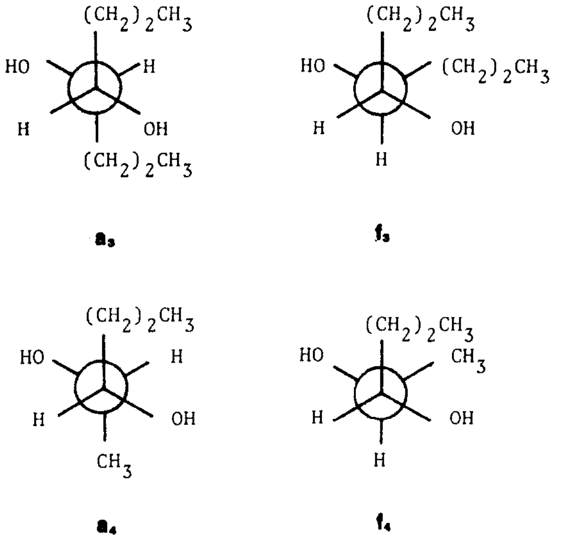
The substitution of Pr (f_3) by a Me group (f_4) decreases the steric interaction so the SR (or RS) isomer is formed and the diastereomer ratio increases (0.66 to 0.95).



Scheme 5.



Scheme 6.



Scheme 7.

In the irradiation of a 2-propanol-2-Me-1-propanol mixture and a 2-propanol-1-propanol mixture only a racemic asymmetric α-glycol was formed in each example. The ^{1}H NMR spectrum of the asymmetric α-glycol $Me_2C(OH)CH(OH)CHMe_2$ is shown in Fig. 4.

At chemical shift values corresponding to Me_2CHCOH group (δ 0.90 to δ 1.10), two doublets appear at δ 0.96 and δ 1.01 and were attributed to the non-equivalent Me groups of the *i*-Pr group. At δ values corresponding to Me_2COH group (δ 1.15 to δ 1.35), two singlets appear at δ 1.21 and δ 1.26 attributed to the original 2-propanol; as it was observed in the corresponding symmetric α-glycol VIII; the bulky *i*-Pr group hinders the rotation around the carbinolic C–C bond. Hence, this asymmetric α-glycol exists in only one conformation in agreement with its very simple ^{1}H NMR spectrum.

Taking into account our formation model of α-glycols and its ^{1}H NMR spectrum we can assume that this glycol could exist in the conformation showed in Scheme 8.

The rigid position of the *i*-Pr group was demonstrated not only by the pair of doublets at δ 0.96 and δ 1.01 but for the methinic proton that appears as well defined doublet at δ 3.22 (J 3.5 Hz) corresponding to a dihedral angle of 60° (Scheme 9).

In the other glycol, *2-Me-2,3-pentanediol*, the *i*-Pr group has been substituted by the smaller Et group, so the other conformations are possible. This result is observed in the ^{1}H NMR spectrum. At δ values corresponding to CH_3CH_2CHOH group (δ 0.85 to δ 1.18), two triplets appear at δ 1.03 and δ 1.08 showing that the glycol exists as a non-interconvertible mixture of two diastereomers. The low resolution of the methinic signal is in agreement with this structure (Fig. 5).

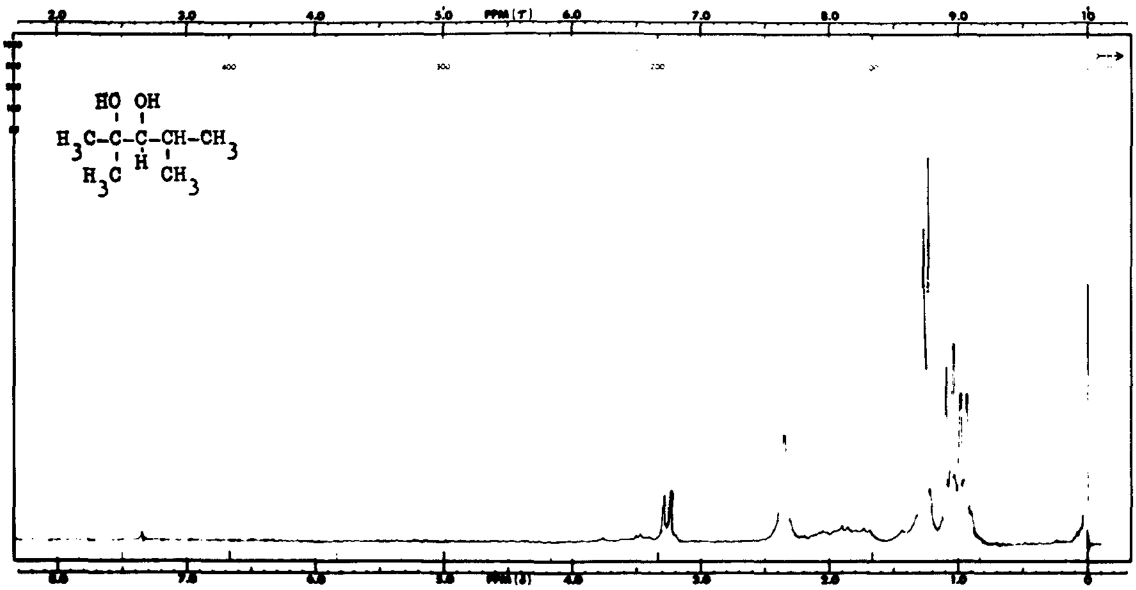


Fig. 4. ^{1}H NMR spectrum of the 2,4-diMe-2,3-pentanediol (XVI).

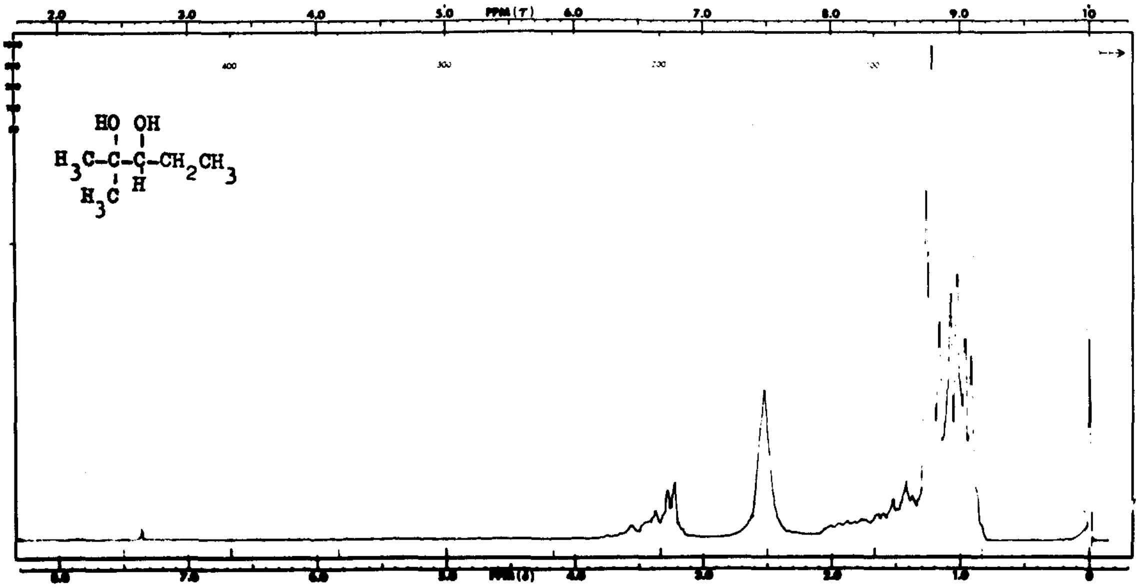
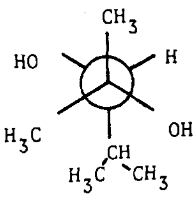
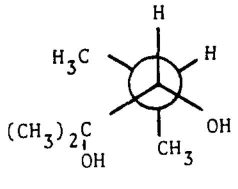


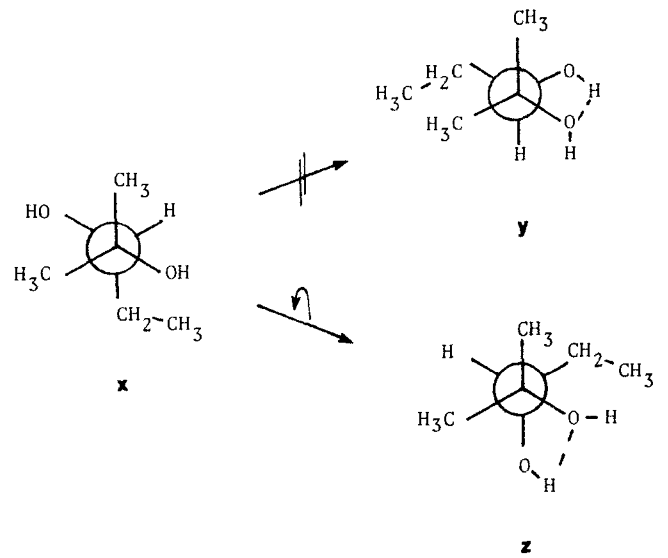
Fig. 5. ^{1}H NMR spectrum of the 2-Me-2,3-pentanediol (XV).



Scheme 8.



Scheme 9.



Scheme 10.

Finally considering the formation mechanism of the symmetric α-glycols, we can assume that the conformer *x* is formed in the first step (Scheme 10) and then a partial rotation is possible (not the one corresponding to the eclipsing of two bulky alkyl groups), to give the conformers *x* and *z*, in agreement with its ^1H NMR spectrum.

EXPERIMENTAL

M.ps are uncorrected and were determined using a Kofler hot-plate apparatus. The UV spectra were determined on a Beckman DK-2A Spectrophotometer and the IR spectra were obtained on a Perkin-Elmer 137 spectrophotometer. The ^1H NMR spectra were recorded on a Varian A-60 spectrometer using TMS as internal standard. The MS were determined on a Varian MAT CH-7 spectrometer at 70 eV. Glc analysis were performed on a: (1) Hewlett Packard Research Gas Chromatograph 5750 B and Hewlett Packard recorder 7127 A and (2) Hewlett Packard Research Gas Chromatograph 5830 A and Hewlett Packard recorder 18850 A. Both instruments were equipped with hydrogen-flame ionization detector, with nitrogen as the carrier gas. Glc analysis were conducted using (i) a column 6 ft × 1.5 mm of 10% Carbowax 6.000 on 80–100 mesh diatomite "W", for alcohols, aldehydes, ketones, acids, symmetric and asymmetric low molecular weight α-glycols, ethers, esters and cyclohexanol; (ii) a column 6 ft × 2 mm of 10% PORAPAK-Q on 80–100 mesh diatomite "W", for alcohols, aldehydes and ketones; (iii) a column 6 ft × 1.8 mm of 10% EGS on 80–100 mesh diatomite "W" for symmetric and asymmetric α-glycols, cyclohexanol, ethers and esters and (iv) a column 6 ft × 1.5 mm of 10% NPGS on 100–120 mesh diatomite "G", for symmetric and asymmetric α-glycols, cyclohexanol, acids and esters.

Compounds used for the photochemical reactions. The aliphatic alcohols employed in this work were "Practical Grade reagents". They were distilled and characterized from their b.p. and ^1H NMR spectra. Glc analysis and IR spectra showed that the carbonyl impurities were absent.

Standard compounds used for the glc analysis. The carbonyl compounds, ethers and esters used as references in glc analysis were purified and characterized as above mentioned. Acetaldehyde, acetone and propanaldehyde were used in tlc as their 2,4-dinitrophenylhydrazones.

bis-*Phenylurethans.* The symmetric α-glycols were characterized by their *bis*-phenylurethans. They were prepared according to methods described by Cheronis.[46] Colorless plates from benzene-petroleum ether. M.ps and ^1H NMR spectra are:

bis-*Phenylurethan from* **I**, m.p. 168° (lit.[9] m.p. 174°); ^1H NMR (Cl_3CD) CH_3 δ 1.32 (d, J 6 Hz); CH 5.04 (m); NH 6.71 (s); C_6H_5 6.85–7.60 (m).

bis-*Phenylurethan from* **II**, m.p. 199° (lit.[47,48] m.p. 199°); ^1H NMR (Cl_3CD) CH_3 δ 1.34 (d, J 6 Hz); CH 5.08 (m); NH and C_6H_5 7.00–7.25 (m).

bis-*Phenylurethan from* **III**, m.p. 134°; ^1H NMR (Cl_3CD) CH_3 δ 0.97 (t, J 6.5 Hz); CH_2 1.55 (m); CH 4.90 (m); NH 6.64 (s); C_6H_5 6.90–7.50 (m).

bis-*Phenylurethan from* **IV**, m.p. 215° (lit.[33] 213°); ^1H NMR (Cl_3CD) CH_3 δ 0.99 (t, J 7 Hz); CH_2 1.65 (m); CH 4.93 (m); NH 6.60 (s); C_6H_5 7.00–7.65 (m).

bis-*Phenylurethan from* **V**, m.p. 249°; ^1H NMR (Cl_3CD) CH_3 δ 1.64 (s); NH and C_6H_5 6.95–7.35 (m).

bis-*Phenylurethan from* **VI**. m.p. 136° (lit.[49] 133°); ^1H NMR (Cl_3CD) CH_3 δ 0.84 (m); CH_2 1.54 (m); CH 5.00 (m); MH 6.83 (s); C_6H_5 6.90–7.55 (m).

bis-*Phenylurethan from* **VII**, m.p. 179° (lit.[50] 191°); ^1H NMR (Cl_3CD) CH_3 δ 0.90 (m); CH_2 1.53 (m); CH 4.95 (m); NH 6.84 (s); C_6H_5 6.70–7.50 (m).

bis-*Phenylurethan from* **VIII**, m.p. 244°; ^1H NMR (Cl_3CD) CH_3 δ 0.95 (d, J 6.5 Hz) and 1.00 (d, J 6.5 Hz); CH 5.00 (m); NH and C_6H_5 6.83–7.35 (m); $(CH_3)_2CH$ 1.73–2.15 (m).

bis-*Phenylurethan from* **XI**, m.p. 259° (lit.[16] 250°); ^1H NMR (Cl_3CD) CH_3 δ 0.92 (d, J 6 Hz); CH_2 1.10–1.80 (m); CH 5.12 (m); NH 6.60 (s); C_6H_5 6.90–7.60 (m); $(CH_3)_2CH$ 1.10–1.80 (m).

General method of irradiation

The aliphatic alcohols were irradiated in the liquid state (50 ml) in quartz Erlenmeyer flasks (100 ml) with stirring. The light source was a Hg high-pressure lamp (Hanau-Quarzlampen, G.M.BH,TQ 150) which was placed at 10 cm from the flask. The progress of the reaction was followed by glc. Irradiation time was 18 hr and the liquid reached a maximum temp of 60–70°.

At the end of the irradiation, usually the glc analysis showed the non-converted starting alcohol peak and three peaks in the following order (increasing values of RR_t): carbonyl compounds, *dl*-α-glycol and *meso*-α-glycol.

The ratio of the diastereomeric α-glycols formed (*dl*/*meso*, Table 1) were calculated from the integrated chromatograms.

The asymmetric α-glycols were obtained when the irradiations were performed, in a similar manner, on alcohols mixtures with a ratio 1:1 (or 3:7, Table 4). The glc analysis showed the presence of products coming from each alcohol (carbonyl compounds and symmetric α-glycols) and one or two very important peaks corresponding to the asymmetric α-glycols.

The ratio of the symmetric α-glycols and asymmetric α-glycols formed and the ratio of the diastereomeric asymmetric α-glycols, when they were formed, were calculated from the integrated chromatograms (Table 4).

When the irradiation was completed the liquid products were isolated from the mixture by distillation through a spinning band column (Nester-Faust, Wilmington, Del., 2912520 31 cm) under reduced pressure. Sometimes an electric heated column was used. The small fractions isolated were analysed by glc and those with the same composition were combined. So, the first fraction which contained the carbonyl compounds was identified from their RR_t and 2,4-dinitrophenylhydrazones. The second fraction was identified as non converted starting alcohol by its RR_t and IR. The third and fourth fractions were identified as *dl*-glycol and *meso*-glycol (Table 2) respectively.

The solid *meso*-glycols were obtained by recrystallization (solv. benzene–EtOH) from the distillation residue.

The asymmetric α-glycols were purified and identified in a similar manner (Table 5). They were obtained from an intermediate fraction between the symmetric α-glycols low b.p. fraction and the symmetric α-glycols high b.p. fraction.

Irradiation of cyclohexanol

The irradiation of liquid cyclohexanol was performed by the same method employed with aliphatic alcohols. The glc analysis showed the non-converted cyclohexanol peak and two important peaks whose RR_t difference were longer than the corresponding one to diastereomeric α-glycols. In the same chromatogram the carbonylic compound (cyclohexanone) showed a RR_t similar to the cyclohexanol. The irradiated liquid was distilled under reduced pressure. The first fraction contained the non-converted starting alcohol (convertion 19%) was identified by glc and IR. From the second fraction, was obtained cyclohexanone (yield 5%) identified by glc and IR. The product from the third fraction was identified as hexanoic acid (yield 37%) by b.p., IR, ^{1}H NMR, MS and RR_t.

Cyclohexyl hexanoate was obtained from the fourth fraction (yield 55%) colorless liquid, b.p. 78° (27 mm) and was compared with an authentic sample[51] (Found: C, 72.46; H, 11.17. $C_{12}H_{22}O_2$ requires: C, 72.68; H, 11.18); IR (film) (cm^{-1}) CH 2850; C=O 1725; CO 1170 and 1240; ^{1}H NMR (Cl_3CD) δ CH_3 0.90 (3H, t, J 6 Hz); CH_2 1.06–2.10 (16 H, m); CH_2–C=O 2.26 (2H, t, J 6 Hz); ROC-H 4.78 (1H, m). MS *m/e*(%) 175(100); 117(50); 115(29); 99(42); 98(50); 82(42); 81(66); 71(25); 69(29); 60(33); 55(58); and 43(50); 41(58). Glc (NPGS), the RR_t was smaller than that corresponding to the hexanoic acid.

The chromatography on alumina of the irradiation products using petroleum ether or mixtures of petroleum ether–benzene and benzene–EtOH as eluants yielded similar results.

Oxidation with HIO_4

The α-glycol (20 mg) was dissolved in a 0.36M soln of HIO_4 (1 ml) and the mixture was left in the dark at room temp for 1 hr. After that time the reaction was complete. The soln was extracted with Cl_3CH, and the carbonylic compounds were separated from the extracts and identified by glc and as their 2,4-dinitrophenylhydrazones derivatives (tlc).

The oxidized α-glycols were: *dl*- and *meso*-2,3-butanediol, *dl*- and *meso*-3,4-hexanediol, pinacol and *dl*-2-Me-2,3-pentanediol.

Thermal stability of α-glycols

The α-glycol (40 mg) was dissolved in Cl_2CH_2 (10 ml) and the soln was heated in the dark at 60–70° for 15 hr. Glc analysis showed that the glycol was stable under these conditions.

Photochemical stability of α-glycols

The α-glycol (40 mg) was dissolved in Cl_2CH_2 (10 ml) and the soln was irradiated in a similar manner as the aliphatic alcohols. The progress of the reaction was followed by glc and interconvertion between the diastereomeric α-glycols was not observed.

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