Tetrahedron Vol 31, pp 441 to 447 Pergamon Press 1975 Printed in Great Britain

FACTORS INFLUENCING STEREOSELECTIVITY IN THE PHOTOREDUCTION OF SOME CYCLOHEXANONES

J. C. MICHEAU, N. PAILLOUS and A. LATTES*
Laboratoire des Composés Azotés Polyfonctionnels, UER de chimie Organique, Université Paul Sabatier, 118, route de Narbonne 31400 Toulouse, France

(*Received in UK* 19 *July* 1974, *Accepted for publication* 7 *October* 1974)

Résumé—La photoreduction des cyclohexanones non substituées en α conduit généralement aux cyclohexanols diastéréoisomères lorsque le photoréducteur est un alcool ou un hydrocarbure. Dans les éthers on isole également des photoadduits. La stéréosélectivité de photoréduction dépend des conditions expérimentales. En particulier dans le propanol-2 elle varie avec le rapport molaire cyclohexanone/propanol-2 avec l'intensité lumineuse incidente et avec l'addition de pièges à radicaux (disulfure de phényle, hexène-1).

Nos résultats peuvent s'interpréter au niveau de l'étape radicalaire. Ils sont discutés en fonction des deux hypothèses d'un centre radicalaire strictement plan ou pyramidal.

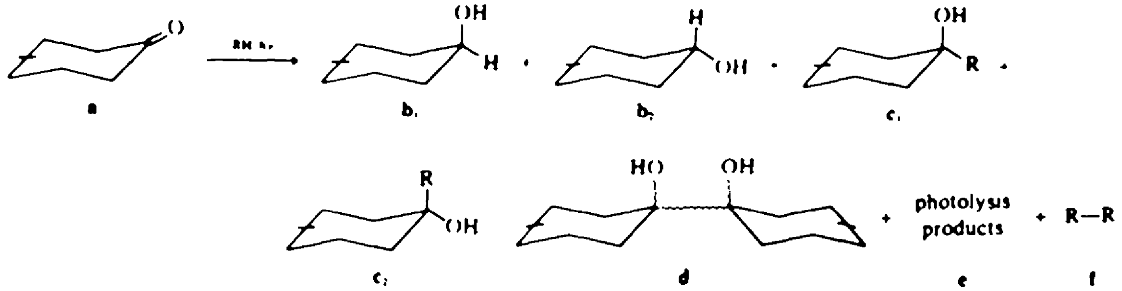
Abstract—Photoreduction of cyclohexanones not α substituted, generally leads to diastereoisomeric cyclohexanols when the hydrogen-donor is an alcohol or an hydrocarbon. In ethers photoadducts are also isolated.

The stereoselectivity of photoreduction depends on experimental conditions. In 2-propanol in particular, it varies with the cyclohexanone/2-propanol molar ratio, with the incident light intensity and with addition of radical scavengers (phenyl disulfide, 1-hexene).

The present results can be interpreted at the radical step. They are discussed according to two assumptions of a strictly planar or pyramidal radical centre.

UNTIL now the stereochemical aspect of cyclohexanone photoreduction has not been extensively investigated. Nevertheless, in a slightly different field, Steneveld[1] reported the formation of optically active ketones during the photoreduction of camphorquinone by cyclohexanols. But Coyle,[2] disregarded this aspect in the photoreduction of 3-methylcyclohexanone in methanol.

As no systematic investigation seemed to have been undertaken, we took up this problem and our preliminary results concerning the photoreduction of variously substituted cyclohexanones were reported in a previous paper.[3] These compounds are easily reduced in hydrogen-donor solvents so long as they are not α substituted. These reactions can be summarized as follows:



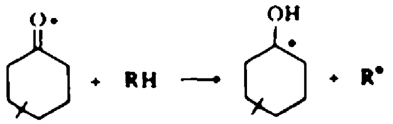
The corresponding diastereoisomeric cyclohexanols (b_1 and b_2) are mainly obtained with good yield (about 90 per cent) and with a stereoselectivity depending upon the experimental conditions.

Also shown is the presence of various coupling products (c_1, c_2, **d**, **f**) in different amounts according to the nature of the hydrogen donor, as well as small quantities of photolysis products (**e**) (Norrish cleavage, type I for example). The presence of coupling products suggests a radical mechanism. Moreover, this type of mechanism is commonly accepted for cyclohexanone photoreduction by 2-propanol[4] as well as for the simultaneous addition reactions.[5]

Nature of the excited state. The n, π^* triplet state of the cyclohexanones is the only one responsible for the photoreduction. Piperylene solutions (10^{-3} or 10^{-4} M) slow down the reaction and a concentration of 0·02 M quenches the reaction. In the same way, a 0·01 M naphthalene solution lowers the quantum yield of photoreduction of a 0·02 M cyclohexanone solution in 2-propanol ($\Phi_0/\Phi = 1{\cdot}1$).[6] All these data, which are consistent with the intervention of a triplet state, are in

---

*Envoyer les épreuves et toute correspondance à M. Lattes, UER de chimie organique, Université Paul Sabatier, 118, route de Narbonne-31077 Toulouse Cedex.



good agreement with accepted facts[*] concerning intermolecular photoreductions.

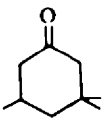
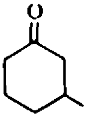
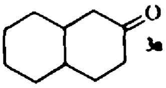
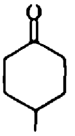
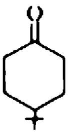
Stereoselectivity of photoreductions and experimental conditions

Stereoselectivity measured from (b_1 and b_2) diastereoisomeric cyclohexanols, depends to a very large extent on the experimental conditions but not on the conversion value in the range 0–40%.

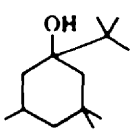
Effect of the molar ratio ketone/hydrogen donor. For the majority of photoreducing agents, especially 2-propanol, and as long as the light intensity remains fairly weak ($I \sim 5 \times 10^{15}$ Q/s) the stereoselectivity is changing markedly when the molar ratio is varying. In every case, the ratio $b_1/b_1 + b_2$ (1,3-*trans*- or 1,4-*cis*-cyclohexanol) is increasing as the ketone/hydrogen-donor molar ratio increases.

As we can see in Table 1,3,3,5-trimethylcyclohexanone **1a** shows the greatest change in stereoselectivity. That is the reason why we chose this ketone for the next step of our investigation.[*]

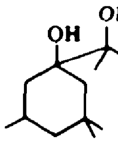
Table 1. Photoreduction in 2-propanol. % of alcohol b_1 vs initial cyclohexanone/2-propanol molar ratio (M.R.)

Ketone	No.	Stereoselectivity $\frac{100b_1}{b_1 + b_2}$	
		M.R. 0.001	M.R. 0.182
	**1a**	32	67
	**2a**	26	38
	**3a**	31	40
	**4a**	21	31
	**5a**	18	27

Effect of the nature of the hydrogen donor solvent. Table 2 shows a distinct change in stereoselectivity as a function of the molar ratio with the majority of solvents except for ethers where the change is non significant. In these solvants, the reduction is in competition with an addition reaction whose relative significance is determined by the ether investigated (addition/reduction = 1/1 with diethylether and 1/4 with diisopropylether respectively) but not by the ketone/ether molar ratio. The structure of the photoadducts was determined when the solvent was diisopropylether. Here we are concerned both with the two diastereoisomeric ether-alcohols **6** in whose mixture, c_1 type isomer is predominant. ($c_1/c_1 + c_2$ = 70%)



6



7

2-propanol adds on cyclohexanones but the yield of the adducts is significant only if the incident light intensity is relatively high.

Effect of light intensity. The previous data led us to investigate the contribution of this factor to the stereoselectivity of reduction and correlatively to the relative amounts of coupling products. For that purpose we decided to work with 2-propanol but similar variations also occur with cyclohexane.

Under the selected experimental conditions (Table 3) the main coupling products were both diastereoisomeric diols **7** wherein the c_1 type isomer was predominant ($c_1/c_1 + c_2$ = 75%).

Small amounts of other compounds were also found with high intensity irradiation. This was probably due to symmetric pinacols **8** (2–5% in the mixture after reaction) together with products whose structure has not been established, but which resulted presumably of further transposition. Table 3 shows that the higher the incident light intensity was, the weaker the cyclohexanol $b_1/b_1 + b_2$ ratio was. Under these conditions (6×10^{16} Q/s) the change in stereoselectivity *vs* ketone/2-propanol molar ratio is small and a large proportion of coupling products is found.

Remark. We have checked that the effects reported in Table 3 could be correlated only with changes in light intensity and not with correlative changes in temperature. When light intensity was constant, the ratio $b_1/b_1 + b_2$ was enhanced from 40 to 56% by raising the temperature from −15° to +60° whilst an increase of light intensity had the reverse effect.

Photoreduction stereoselectivity and radical scavengers

The previous results show that in all cases where the change in stereoselectivity *vs* molar ratio was small (ethers or 2-propanol under relatively intense irradiation...) a correlated high ratio of photoadducts could be found. It suggested that the addition can be related to the

Table 2 Photoreduction of ketone 1a in various solvents: $1b_1/1b_1 + 1b_2$(%)

Hydrogen-donor M R	2-Propanol	Cyclohexane	Hexane	Methanol	2-Octanol	i-PrOiPr	EtOEt	MeOiPr
0·001	32	32	33	48	45	33	34	27
0·182	67	52	50	60	54	36	36	27

Table 3 Variation in the c/b ratio and photoreduction stereoselectivity vs incident light intensity (ketone 1a: 0·05 M in 2-propanol)

Incident light intensity (Q/s)	$1b_1/1b_1 + 1b_2$ (%)	addition/reduction (c/b) %
6×10^{16}	41	15
$0·3 \times 10^{16}$	46	4
$0·02 \times 10^{16}$	54	2

photoreduction stereoselectivity. Since the two processes compete from the same radical species, we examined the role of radical scavengers during the reaction process.

We used successively H compounds which affect hydrogen transfer reactions and scavengers which add directly to the radicals.

Effect of carbonyl compounds. Ketones themselves can be considered as radical scavengers. In fact, it is known[10,11] that they react with ketyl radicals and cause a hydrogen transfer reaction.

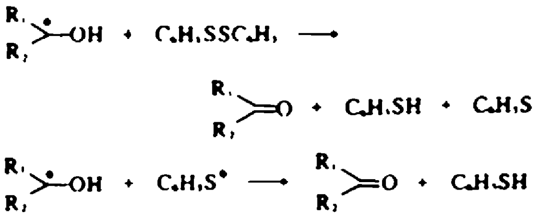
The addition of carbonyl compounds had the same effect on stereoselectivity as an increase of the cyclohexanone/hydrogen donor molar ratio. However the quantum yield of photoreduction of ketone 1a in 2-propanol was not changed by a further addition of a photoreducible or non-photoreducible cyclohexanone (5a, cyclohexanone, 2-méthyl-cyclohexanone) (Table 4). Moreover, the photoreduction quantum yield of a cyclohexanone by 2-propanol can be generally regarded as independent of the addition of a new cyclohexanone compound.

A significant increase can be observed in the $b_1/b_1 + b_2$ ratio of cyclohexanol which ever type of cyclohexanone was photoreduced.

Table 4 Photoreduction quantum yield of ketone 1a upon addition of 2-methylcyclohexanone (2-propanol 7·75 M)

Ketone 1a (M)	2-Methylcyclohexanone (M)	Φ red
0·98	0	0·27
0·98	0·50	0·28

Effect of phenyl disulfide. The scavenging effect of phenyl disulfide may be understood from the following reactions:[12]



The photoreduction quantum yield of ketone 1a in 2-propanol was halved upon addition of 3×10^{-4} M phenyl disulfide. As in the previous case the $b_1/b_1 + b_2$ ratio of alcohol increases.

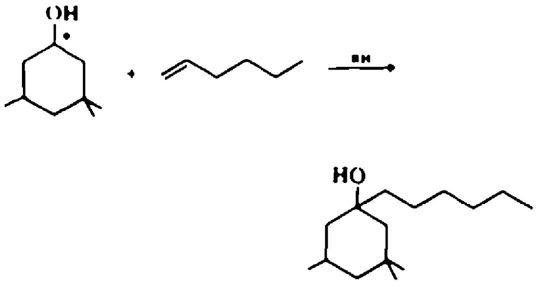
Remark. The stereoselectivity change observed upon adding carbonyl compounds or phenyl disulfide is not related to any inner filter effect. Such a stereoselectivity change induced by a mere intensity variation would require indeed a much lower intensity (I/100), whereas the real change factor is only one half.

Table 6 Photoreduction stereoselectivity of ketone 1a (0·09 M) in 2-propanol upon addition of phenyl disulfide (I ~ 5×10^{16} Q/s)

ΦSSΦ(M) $\times 10^4$	Cyclohexanol $1b_1$ (%)
0	44
1·22	49
2·44	54

Table 5 Competitive photoreduction of ketones 1a and 5a in 2-propanol (I ~ 5×10^{16} Q/s)

Ketone 1a: 0·03 M		Ketone 5a: 0·02 M	
Ketone 5a (M)	Cyclohexanol $1b_1$ (%)	Ketone 1a (M)	Cyclohexanol $5b_1$ (%)
0	39	0	17
0·01	48	0·02	21
0·05	59	0·04	24
0·07	65	0·07	29
0·16	73	0·11	32



9

Table 7 Photoreduction stereoselectivity of ketone 1a (initial concentration 0·53 M) in presence of a diluting agent

	Cyclohexanol $1b_1/1b_1 + 1b_2$ (%)	
Diluting agent (%)	1-hexene	benzene or *t*-BuOH
0	65	65
10	62	65
20	57	64
30	54	62
40	50	60

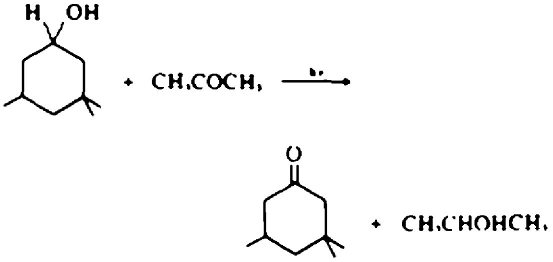
Effect of 1-*hexene*. The addition of 1-hexene slows down the photoreduction of ketone 1a in 2-propanol. Here, it is not a dilution effect, for the addition of a diluting agent, which does not absorb at 300 nm (*t*-BuOH, C_6H_6) does not actually change the photoreduction time (for a 10 per cent conversion) before there is a 50 per cent dilution. Under these conditions, the addition of 1-hexene to the 3,3,5-trimethylhydroxycyclohexyl radical[11] gave 1-hexyl 3,3,5-trimethylcyclohexanol 9

It was mainly a c_1 type diastereoisomer. Stereoselectivity is varying according to these additions: slightly with inert diluting agents and more significantly with 1-hexene. In every case, the $b_1/b_1 + b_2$ ratio of cyclohexanol decreased. In short, the stereoselectivity changes can be rationalized on the basis of the effects produced by the moieties interacting with the radical. Those which occur at the hydrogen transfer step increase the $b_1/b_1 + b_2$ ratio (carbonyl compounds, phenyl disulfide) and those, which react with the hydroxycyclohexyl radical at the *p* orbital (1-hexene, solvent), lower this ratio

DISCUSSION

The investigation of the stereoselectivity variation process allows us to deal with the problem of the origin of the stereoselectivity itself. We can consider the possible intervention of two $n\pi^*$ excited states. (The irradiation wavelength used—300, 310 nm—corresponds to the $n\pi^*$ absorption band of cyclohexanones.[14] Nozaki *et al.*[15] showed that the stereoselectivity of intramolecular photoreduction of macrocyclic cyclanones depends upon the multiplicity of the excited state concerned. Our quenching experiments allow this assumption to be neglected since addition of piperylene quenches any reaction even at a 0·02 M concentration. Furthermore lower concentrations of piperylene (10^{-3} and 10^{-4} M) do not induce any stereoselectivity variation.

In the same way, we can exclude any involvement of a reverse reaction of selective photooxydation of diastereoisomeric cyclohexanols.



This photooxidation stereoselectivity is in fact very marked, since the cyclohexanol $1b_1$ is oxidized 13·5 times faster than its diastereoisomer $1b_2$ but the trend of the variation as a function of the molar ratio is not consistent with this assumption: it is in mixtures where ketone is the most abundant that the $1b_1/1b_1 + 1b_2$ ratio of cyclohexanol is the highest.

Ruling out these paths, the origin of stereoselectivity must be related with the geometry of the hydroxycyclohexyl radical, this radical being a precursor of the cyclohexanols,† either it is planar or pyramidal. However this assumes that the activation energy for the hydrogen abstraction is smaller than or of the same magnitude order as the activation energy required for radical inversion. According from a given geometry for these transition radical species, various assumptions can be put forward.

Planar radical centre

The radical centre of hydroxycyclohexyl species may be considered planar as suggested by Gritter and Albers[18] to explain the results of radical reaction between 1-octene and diastereoisomeric 4-*t*-butylcyclohexanols ($5b_1$ and $5b_2$) in the presence of peroxides.

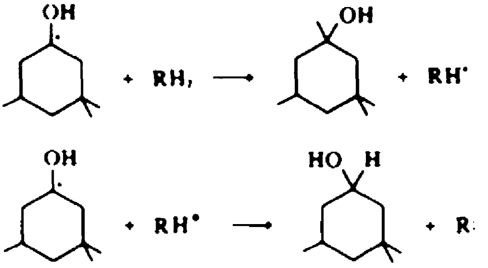
Under this assumption the stereoselectivity changes may be explained: (a) by the competition between several reducing agents, or (b) by different mechanisms which involve free or caged radicals, or (c) by the existence of a conformational equilibrium of the cyclohexane ring, or (d) finally by the participation of solvated species with different steric hindrances.

A. *Participation of several reducing agents.*[17] In the particular case of 2-propanol we can expect that the reduction of the hydrocyclohexyl radical proceeds through either the solvent itself or the hydroxyalkyl radicals.

So that the two reduction processes lead to different alcohols. It is to be assumed that the cyclohexanol $1b_2$, predominant when the cyclohexanone/2-propanol molar ratio is low, arises from reduction by 2-propanol

---

†We have shown that under our experimental conditions pinacols are relatively stable and do not lead to diastereoisomeric cyclohexanols



Reciprocally, the cyclohexanol **1b**$_1$, whose proportion increases with the molar ratio, can be correlated with intervention of hydroxyalkyl radicals. Any radical scavenger addition should decrease the proportion of cyclohexanol **1b**$_1$, whereas, on the contrary, a rise of light intensity would increase the stationary concentration of the radicals. In each case, the reverse effect was experimentally found. (Tables 3 and 4).

B. *Cage effect.*[18] It is also possible that two competitive reactions, either inside a solvent cage or out of the cage, occur. Each one leads to different diastereoisomeric ratios. In fact, the addition of inert solvents with different viscosities, like benzene or *t*-butyl alcohol, has a similar effect. There again, the various radical scavengers used (1-hexene, phenyl disulfide) had not the same behaviour (Tables 6 and 7).

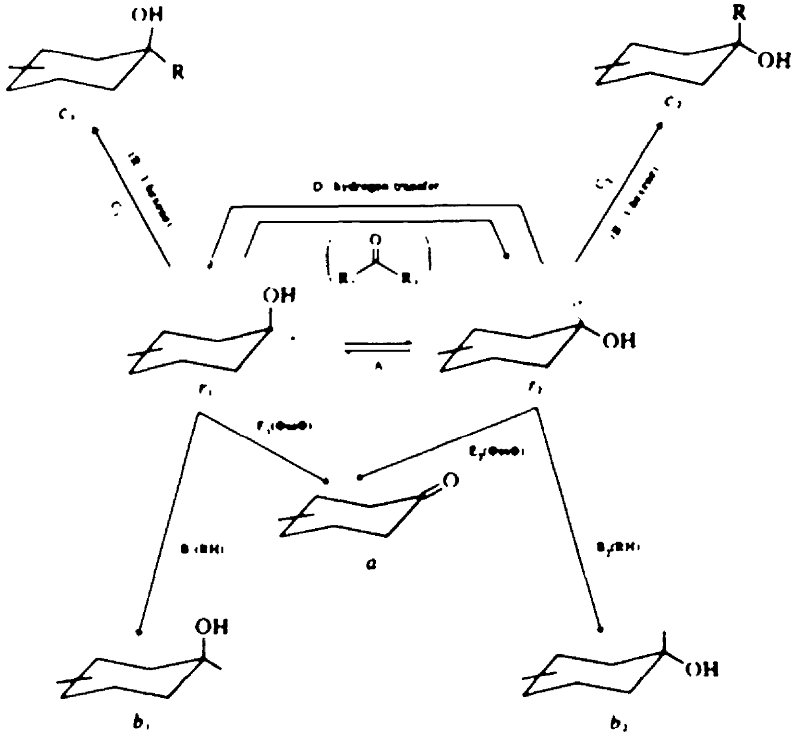
C. *Conformational equilibrium in hydroxycyclohexyl ring.* The participation of a twisted form is put forward by Landor and Regan[19] to explain the particular stereoselectivity of the reduction of ketone **1a** by metallic hydrides. As regards the hydroxycyclohexyl radical[20] the more or less important intervention of such a conformation might explain the stereoselectivity variations in the case of ketones **1a**, **2a**, **4a** but not in the case of ketones of rigid conformation (**3a** and **5a**).

D. *Solvated radicals.*[21] It can also be suggested that both faces of the hydroxycyclohexyl radical are differently solvated by the cyclohexanone or by the hydrogen donor solvent. It is likely that the less hindered equatorial side is preferentially solvated. In such a case, the formation of cyclohexanol **1b**$_2$ which proceeds through axial approach of the hydrogen donor, is favored. When the molar ratio ketone/hydrogen donor is increased, solvation by the photoreducing agent becomes less important and an increase in the cyclohexanol **1b**$_1$ proportion is observed.

The trend in the stereoselectivity change is consistent with this assumption, however the relative importance of solvation is not known and it is not easy to explain why a further cyclohexanone addition changes significantly the stereoselectivity (Table 5) whilst a cosolvent has only a slight effect. (Table 7). This difference may reflect the existence of different solvation types. Thus, an intervention of solvation or association is likely to explain reported variations. However solvation, possibly, is only one parameter in a more complex process. Other effects can also induce stereoselectivity variations and therefore the possible participation of pyramidal radicals was also investigated.

Pyramidal radical centre

It could be suggested that the radical, from its geometry, bears stereochemical information.



Such a possibility is supported by numerous reports. Some ESR studies have provided clear cut evidence for pyramidal radical structures[22-25] in particular for the hydroxyisopropyl radical.[26] The calculations of Fujimoto and Fukui[27] predicted, that the 2-norbornyl radical was slightly pyramidal. Such structures are also involved in the interpretation of reactional mechanisms.[28-30]

Participation of two pyramidal hydroxycyclohexyl radicals. Assuming that the radicals concerned are not planar two radicals species r_1 and r_2 (diagram I) are possible.

These radicals can to undergo, inversion (A, D), reduction (B), addition (C) or oxidation (E) reactions. In the particular case of 3,3,5-trimethylcyclohexanone **1a**, the presence of an axial 3-Me group promotes equatorial attack. The main reaction is photoreduction (B).

On the basis that activation energy is smaller for hydrogen abstraction than for radical inversion, the stereoselectivity of cyclohexanol **1b** can be correlated with the ratio of the populations r_1 and r_2.

All the stereoselectivity variations can be then rationalized by assuming that the previously mentioned reagents can be classified in two groups:

(a) those which react upon the OH group (carbonyl compounds, phenyl disulfide) attack more readily the radical **1r₂**; their action thus increases the **1b₁/1b₁ + 1b₂** ratio of cyclohexanol.

(b) those which conversely, like 1-hexene or the radicals issued from the solvent, attack more readily the radical **1r₁** and thus provide an increase in the ratio **1b₂/1b₁ + 1b₂**. The slight stereoselectivity variation observed in ethers or in 2-propanol under strong light intensity can be explained by competition between hydrogen transfer (D) reduction (B) or addition (C) reactions.* (Tables 2 and 3).

Dilution by means of a consolvent is likely to promote a spontaneous inversion (monomolecular reaction) rather than reduction, addition and hydrogen transfer reactions (bimolecular reactions) (Table 7).

If this assumption seems in good agreement with our data, three critical points must be discussed.

(a) the radical may be only slightly bent—In this case, its effect would not be very important. (b) at room temperature some spontaneous inversion may occur. Some work on similar radicals have shown there is some loss of configuration in these conditions.

(c) at last, it is known that the axial attack of radicals is often preferential because reactivity is so high that the transition state is not very shifted along reaction coordinate and steric hindrances are not very efficient.

In summary, both assumptions (solvation or association, and pyramidal radical centre) can be involved to explain reported results. But we cannot exclude any of these two interpretations or their simultaneous involvement.

EXPERIMENTAL

Materials. Solvents were purified by classical methods: special care was taken in purification of 2-propanol (bidistillation on magnesium shavings) transmission 97% at 250 nm. The cyclohexanones were bidistilled on a Büchi spinning band column: the 4-*t*-butylcyclohexanone **5a** was purified by successive recrystallizations in the water-alcohol system (m.p. 48°), the *trans*-2-decalone **3a** was obtained by preparative GLPC from industrial 2-decalone (Carlo Erba, column device ucon polar 10%, KOH 10% on chromosorb W 30/60 5 meters long, *t* = 135°, Flow 140 ml/mn (column P) n_D^{25} – 1.4810 *trans* authentic n_D^{25} 1.4809.

Apparatus and methods. Three types of apparatus are used to carry out irradiation

(a) a photochemical reactor "Rayonet" Model R.P.R. 100 with 16 RPR 3000 Å lamps and a rotating circular turntable where the various sample are placed. The light intensity variations were obtained in varying the number of lamps or by adequate sized screens.

(b) a quartz photochemical reactor with a Hanovia 450 W medium pressure mercury lamp with a water cooling sleeve. The solutions were degassed by R N_2 bubbling. The temp. changes were obtained by an outside circulation of a thermostatic fluid.

(c) a system analogous to the previous one has a quartz sleeve containing a filtering soln (SO_4Co, $7H_2O$ 220 g/l – $KCr(SO_4)_2$, $12H_2O$ 60 g/l 1 = 1 cm) and (K_2CrO_4 0.1 g/l + Na_2CO_3 1% 1 = 0.6 cm) isolating the 3130 Å line $\Delta\lambda$ = 40 nm I ~ 0.6 × 10¹⁸ Q/s. A turntable of 12 cm in diameter supports the samples.

The ketone solns (3.5 Me) were placed in pyrex tubes and degassed before irradiation by the freeze thaw method: three identical cycles to about 10^{-3} torr were carried out. These tubes were then vacuum sealed (with quartz tubes, degassing was achieved by means of an inert gas bubbling).

Stereoselectivity was measured at 10 per cent in reaction progress (column ucon polar 3%, KOH 6%, on chromosorb W 60/80, 4.5 meters long *t* = 110°, flow 25 ml/mn column A). In each case the measurements were confirmed by PMR spectra. Quantum yields were measured within the apparatus (c) using the benzophenone/benzhydrol and ferrioxalate systems as actinometers. For chromatographic analysis (column A) 2-octanol was added as an internal standard.

Syntheses and structural determinations. The PMR spectra were carried out at 60 MHz in $CDCl_3$ with addition of neutral anhyd alumine (Varian T 60 internal reference TMS). The mass spectra were recorded on a quadrupolar QSM apparatus (ionisation energy 70 eV) and the IR spectra on a Beckman IR 20 apparatus, only characteristics signals are indicated. The photochemical syntheses of the tertiary alcohols were carried out within the apparatus (b).

2-(1-*Hydroxy-3,3,5-trimethylcyclohexyl*)2-*isopropoxypropane* (**6**). A 0.4 M soln of **1a** in diisopropylether was irradiated until complete disappearance (24 hr) yield 25%. Then the alcohols **6** were isolated by preparative GLPC (column P) *t* = 130°, r.t. = 35 mn. PMR ppm δ = 3.82 (1H septuplet, *J* = 6 Hz CH isopropyl), δ = 2.60 (1H OH) analysis of this signal showed a weak field multiplet and a high field doublet in the 30/70 ratio attributed to the diastereoisomers c_2 and c_1 respectively.[31] This ratio was consistent with analytical GLPC data. Mass *m/e* 209 (M-33), 141, 123, 101, 83.

2-(1-*Hydroxy-3,3,5-trimethylcyclohexyl*) 2-*hydroxypropane* (**7**). A 0.4 M soln of **1a** in 2-propanol was irradiated in a quartz sleeve until complete disappearance, yield 15%. The diols **7** were isolated by preparative GLPC (column P) *t* 150°, r.t. = 45 mn. PMR ppm δ ~ 2.60 (1H singlet OH of lateral chain), δ – 2.20 (1H OH of the ring), analysis of the latter multiplet showed a badly resolved doublet in the 25/75 ratio ($CDCl_3$)-well separated in C_6H_6-corresponding to both diastereoisomer c_2 and c_1

---

*Gritter and Albers[18] observed the same stereoselectivity upon addition of 1-octene on both radicals 4-*t*-butylhydroxycyclohexyl issued from two diastereoisomeric cyclohexanols. This reflected presumably a fast inversion of the radical in their experimental conditions (predominantly reaction A).

(consistent with GLPC) Mass m/e 182 (M-18), 164, 149, 141, 123, 59, 55. IR Film 3450, 2940, 1455, 1365 and 1175 cm^{-1}

1-*Hexyl-3,3,5-trimethylcyclohexanol* (**9**) A 0.4 M soln of **1a** was irradiated in a 50/50 mixture of 2-propanol/1-hexene until 50 per cent conversion (~200 hr), yield 20 per cent Alcohols **9** were further isolated by preparative GLPC (column P) t = 130°, r t = 35 mn This compound was also obtained by chemical means (by action of magnesium hexyl bromide on **1a** (isomer e_1 > 90%[32]) and purified by preparative GLPC (same conditions) The spectrographic data are identical whichever method preparation was used PMR δ = 1.30 (13 H, n-hexyl) Mass m/e 208 (M-18), 141, 123, 83. IR Film 3450, 2930, 2915, 2855, 1450, 1355, 1020 cm^{-1}

The symmetric pinacols of the cyclohexanone **10** and of the ketone **1a** **8** were synthesised by the Wineman technique ($HgCl_2/Mg$)[31]

1-(1 *Hydroxy-1-cyclohexyl*) 1-*hydroxycyclohexane* (**10**) Mass m/e 180 (M-18), 161, 99, 81 m p = 131 lit[33] 130°

1-(1-*Hydroxy-3,3,5-trimethylcyclohexyl*) 1-*hydroxy-3,3,5-trimethylcyclohexane* (**8**) Mass m/e 264 (M-18), 245, 141, 123, 83 m p 154°

The symmetric pinacol of the cyclohexanone **10** was identified in the irradiated mixtures cyclohexanone/2-propanol and the pinacols **8** in the mixtures ketone **1a**/2-propanol However stereochemical problems made structural determination of various isomers difficult.

The photochemical stability of pinacols **7** and **8** was checked, pinacol **7** or **8** was added to a soln (0.05 M) of cyclohexanone in 2-propanol (0.02 M) and the degassed mixture was irradiated until disappearance of initial cyclohexanone Under these conditions it was not possible to detect by analytical GLPC any **1b** resulting from an eventual cleavage of pinacol **7** or **8**

REFERENCES

[1] K Steneveld, *Diss Abstr* Int B, 31(9), 5273 (1971)
[2] J D Coyle, Ph.D Thesis, Oxford University (1969)
[3] J C Micheau, N Paillous and A Lattes, *Tetrahedron Letters* 637 (1972)
[4] R Simonaitis, G W Cowell and J N Pitts, Jr *Ibid* 3751 (1967)
[5] N J Turro and D M McDaniel, *Mol Photochem* 2(1), 39 (1970)
[6] W M Moore and M Ketchum, *J Am Chem Soc* **84**(8), 1368 (1962)
[7] J. C Scaino, *J Photochem* **2**, 81, (1973/74)
[8] J Kossanyi and B Furth, *L'actualité chimique* **2**, 7 (1974) et 3, 3 (1974)
[9] J P Quintard and M Pereyre, *Bull Soc Chim Fr* 5, 1950 (1972)
[10] B M Monroe and S A Weiner, *J Am Chem Soc* **91**(2), 450 (1969)
[11] J P Morizur, B Furth and J Kossanyi, *Bull Soc Chim Fr* 5, 1959 (1970)
[12] S G Cohen, S Orman and D A Laufer, *J Am Chem Soc* **84**, 3905 (1962)
[13] W H Urry, F W Stacey, F S Huyser and O O Juveland, *Ibid* **76**, 450 (1954)
[14] O L Chapman and D S Weiss, *Org Photochem* 3, 197 (1973)
[15] K Matsui, T Mori and H Nozaki, *Bull Chem Soc Japan* **44**, 3440 (1971)
[16] R J Gritter and R J Albers, *J Org Chem* **29**, 728 (1963)
[17] B Rickborn and M T Wuesthoff, *J Am Chem Soc* **92**(23), 6894 (1970)
[18] S A Weiner, *Ibid* **93**(2), 425 (1971)
[19] S R Landor and J P Regan, *J Chem Soc* (C), 1158 (1967)
[20] C Corvaja, G Giacometti and M Brustolon, *Z Phys Chem* **82**, 272 (1972)
[21] C Walling, *Bull Soc Chim Fr* 4, 1609 (1968)
[22] A J Dobbs, B C Gilbert and R O C Norman, *Chem Comm* **23**, 1353 (1969)
[23] T. Kawamura, T Koyama and T Yonezawa, *J Am Chem Soc* **92**(24), 7222 (1970)
[24] J Gloux, M Guglielmi and H Lemaire, *Mol Phys* **19**(6), 833 (1970)
[25] S O Kobayashi and O Simamura, *Chem Letters* 699 (1973)
[26] B C Gilbert, *Electron Spin Resonance* 1, 205 (1972)
[27] H Fujimoto and K Fukui, *Tetrahedron Letters* **45**, 5551 (1966)
[28] J B Guttenplan, *Diss Abstr Int B* 31(3), 1162 (1970)
[29] M Gruselle and D Lefort, *Tetrahedron* **29**, 3035 (1973)
[30] S O Kobayashi and O Simamura, *Chem letters* 695 (1973)
[31] R J Wineman, U S Pat 3 113 422
[32] Y Koudsi and Y Maroni-Barnaud, *C R Acad Sci Paris Ser C*, **275**, 427 (1972)
[33] S R Landor, P W O'Connor, A R Tatchell and I Blair, *J Chem Soc* Perkin Trans I, 473 (1973)