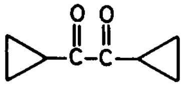
Tetrahedron Letters No. 46, pp 4061 - 4064, 1975. Pergamon Press. Printed in Great Britain.

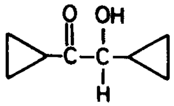
SUBSEQUENT REACTIONS WITHIN ONE AND THE SAME SOLVENT CAGE. THE PHOTOCHEMICAL FORMATION OF 1,2,3-TRICYCLOPROPYL-2-HYDROXY-1,3-PROPANEDIONE FROM CYCLOPROPANECARBALDEHYDE

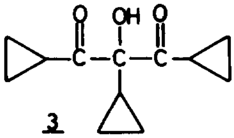
C.W. Funke and H. Cerfontain*
Laboratory for Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129, Amsterdam, The Netherlands

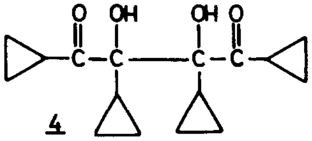
(Received in UK 29 August 1975; accepted for publication 6 October 1975)

The 310 nm irradiation[1] of cyclopropanecarbaldehyde (AH, 1M) in inert solvents[2] yields as major products butanal (1), dicyclopropylethanedione (DK), 1,2-dicyclopropylhydroxyethanone (2) and 1,2,3-tricyclopropyl-2-hydroxy-1,3-propanedione (3). *E.g.* irradiation of 0.7M AH in neopentane at -10° yields these products in a ratio of 4:3:5:2 respectively. Similarly, 1,2,3-tricyclobutyl-2-hydroxy-1,3-propanedione is eventually a major photoproduct on > 300 nm irradiation of cyclobutanecarbaldehyde in inert solvents at -60° [2]. The (unexpected) formation of 3 has to proceed via a multi-step mechanism, since a collision between three cyclopropanecarbaldehyde molecules, one of which is electronically excited, is statistically unlikely.


DK


2


3


4

In order to obtain mechanistic information, a detailed study on the formation of 3 from AH was made. The results are compiled in the Table. In all irradiations 3 and 4 are major products.

The product formation of exp. I, monitored with g.l.c., revealed i) that 1, 2 and DK are primary products, ii) that 3 is formed after an induction period, and iii) that the formation of 3 occurs at the expense of DK. Thus DK is involved in the formation of 3. Kelder and Cerfontain showed that photoexcited DK easily abstracts the methine-H of 2-propanol[3]. For the present system we suggest a similar step, *viz.* abstraction of the loosely bonded acyl-H of AH by photoexcited DK (i), followed by combination of the thus formed radical pair (ii). The result of exp. II supports this proposal.

$$DK^{*} + AH \longrightarrow \overline{DKH^{\bullet}\ \ {}^{\bullet}A} \qquad (i)$$

$$\overline{DKH^{\bullet}\ \ {}^{\bullet}A} \longrightarrow 3 \qquad (ii)$$

$$AH^{*} + DK \longrightarrow AH + DK^{*} \qquad (iii)$$

Exp.	Starting compounds, mole.l^{-1}			Solvent	λ,nm^{1}	T, °C	Product ratio
no	AH	DK	biphenyl				3/4 ^{a}
I	0.7	0 ^{b}	0	neo-C_5H_{12}	310	-10	>10
II	1.0	0.15	0	C_6H_6	403 ^{c}	20	3 ± 1
III	1.0	0.15	0	C_6H_6	310 ^{d}	20	5 ± 1
IV	0.5	0 ^{b}	0	i-PrOH	310	-90	>10
V	1.0	0.15	0	i-PrOH	403 ^{c}	20	< 0.05
VI	1.0	0.15	0	i-PrOH	310 ^{d}	20	1.0 ± 0.2
VII	1.0	0.15	1	i-PrOH	310 ^{d}	20	1.0 ± 0.2

a) for the formation of 4, *vide infra*.

b) DK is formed as a product, $[DK]_{max} \simeq 0.01$ M.

c) only DK absorbs the UV radiation.

d) AH absorbs ≃ 87% and DK ≃ 13% of the UV radiation.

In exp. I only about 1% of the UV radiation is absorbed by DK ($c < 0.01M$, $\epsilon_{310} \simeq 10^{4}$) and 99% by AH ($c \simeq 1M$, $\epsilon_{310} \simeq 10^{5}$). Thus direct excitation of DK cannot account for the high yield of 3.

The energies of the S_1 and T_1 states of AH (84 and 78 kcal.mole^{-1} respectively[6,7]) and of DK (61 and 55 kcal.mole^{-1} respectively [6,8]) show that both the singlet-singlet and triplet-triplet energy transfers are strongly exothermic, and thus probably diffusion controlled[8] (for benzene and 2-propanol as solvent, the energy transfer rates are 16×10^{9} and 5×10^{9} mole.l^{-1}.s^{-1} respectively[9]). Thus prior to steps (i) and (ii), energy transfer (iii) will take place.
The results of the exp. III are in agreement with the proposed energy transfer (iii). The products 1 and 2 are now absent. This shows that the energy transfer (iii) is fast relative to the formation of 1 and 2 from AH*.

The nearly exclusive formation of 4 in exp. V could be anticipated from a study by Kelder and Cerfontain[3], who observed that 4 is the only product (besides acetone) of the 403 nm irradiation of DK in 2-propanol (RH). They explained their results by the steps (iv) - (vii). The very low 3/4 ratio in exp. V indicates that directly excited DK* will abstract hydrogen rather from 2-propanol (step (v)) than from AH (step (i)), as could be expected on the basis of the relative concentrations of the two H-donors (13M *vs* 1M).

$$DK + h\nu \longrightarrow DK^{*} \qquad \text{(iv)}$$
$$DK^{*} + RH \longrightarrow DKH^{\bullet} + {}^{\bullet}R \qquad \text{(v)}$$
$$R^{\bullet} + DK \longrightarrow CH_3COCH_3 + DKH^{\bullet} \qquad \text{(vi)}$$
$$2\ DKH^{\bullet} \longrightarrow 4 \qquad \text{(vii)}$$

The 3/4 ratio of unity obtained in exp. VI is at least 20 times that of exp.

V. In exp. VI DK is excited mainly by energy transfer from AH^*, and only for a small part directly. Apparently *sensitized* DK^* prefers H-abstraction from AH (step (i)) to H-abstraction from 2-propanol (step (v)), especially on considering the concentrations of the two H-donors. This preference can be explained in terms of H-abstraction by DK^* from *the same molecule of AH which transferred its energy to DK*; *i.e.* it occurs before these two molecules diffuse apart. This diffusion will be slower at -90° than at 20°. This is in fact reflected in the higher *3/4* ratio at -90° (exp. IV) than at 20° (exp. VI).

A priori, four different routes for the formation of *3* must now be considered, *viz.* (1-3-7-10), (1-3-8-9-11), (1-2-5-9-11) and (1-4-6-9-11). The superscripts

$$\begin{array}{lcll}
AH + h\nu & \longrightarrow & AH^1 & (1)\\
AH^1 & \longrightarrow & AH^3 & (2)\\
AH^1 + DK & \longrightarrow & AH + DK^1 & (3)\\
AH^1 + DK & \longrightarrow & [AH....DK]^1_{\text{exciplex}} & (4)\\
AH^3 + DK & \longrightarrow & AH + DK^3 & (5)\\
[AH....DK]^1_{\text{exc.}} & \longrightarrow & AH + DK^3 & (6)\\
DK^1 + AH & \longrightarrow & \overline{DKH^\bullet \quad {}^\bullet A}^{\,1} & (7)\\
DK^1 & \longrightarrow & DK^3 & (8)\\
DK^3 + AH & \longrightarrow & \overline{DKH^\bullet \quad {}^\bullet A}^{\,3} & (9)\\
\overline{DKH^\bullet \quad {}^\bullet A}^{\,1} & \longrightarrow & \underline{3} & (10)\\
\overline{DKH^\bullet \quad {}^\bullet A}^{\,3} & \longrightarrow & \underline{3} & (11)\\
AH^3 + BP & \longrightarrow & AH + BP^3 & (12)\\
BP^3 + DK & \longrightarrow & BP + DK^3 & (13)
\end{array}$$

1 and 3 denote the multiplicity of either an electronically excited state or an intimate radical pair.

The result of exp. VII rules out route (1-2-5-9-11). The energies of the S_1 and T_1 state of biphenyl (97 and 65 kcal.mole^{-1} [8]) relative to those of AH (*vide supra*) render biphenyl an efficient and selective quencher of AH^3. The presence of biphenyl (BP) will therefore affect route (1-2-5-9-11) as the triplet energy transfer to BP (step (12)) will be about seven times (*viz.* 1M/0.15M) as efficient as to DK (step (5)) assuming both steps to be diffusion controlled[8]. The thus formed BP^3 will, in its turn, transfer its energy to DK (step (13)). Based on the T_1 energies of BP and DK (*viz.* 65 and 55 kcal.mole^{-1} [8]) step (13) will be diffusion controlled with a rate of $k.[DK].[BP] = 5.10^9[BP]\text{mole}.l^{-1}.s^{-1}$ and will thus be dominating over the radiationless decay of BP^3 which will have a much lower rate (*cf.* [10]). It is evident, that the DK^3 formed via (1-2-12-13) will behave, as for H-abstraction from AH or RH, like *directly*, *i.e.* photo-excited DK and thus would mainly yield *4*. In fact, this is not observed, thus ruling out route (1-2-5-9-11). Route (1-3-8-9-11) is also rather unlikely, since the collision pair of AH and DK^1 formed in step (3) will have a lifetime of 10^{-11}s [11] which is too short to allow for step (8) ($k_8 \simeq 10^8 s^{-1}$ [12]). In other words, diffusion of the partners of the collision pair of AH and DK^1 will be fast relative to step (8).

This objection does not hold for route (1-4-6-9-11), as the exciplex association will delay the diffusion which may now be slower than step (8).

The preferred formation of <u>4</u> in the photolysis of AH may thus be explained by the routes (1-3-7-10) and (1-4-6-9-11) between which as yet no distinction can be made.

Acknowledgement

We thank Mr. J.A.J. Geenevasen for his part of the experimental work and Dr. J. Kelder for a gift of dicyclopropylethanedione. This work was carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) and with financial support from the Netherlands Organization for Advancement of Pure Research (Z.W.O.).

Notes and references

1. The photolyses were carried out in pyrex vessels, either in a Rayonet photochemical reactor with 300 nm lamps, the intensity of the transmitted light being maximal at 310 nm, or with a Philips SP-500 W mercury lamp, combined with a 403 glass filter (PAL no. 80332.03).
2. C.W. Funke, J.A.J. Geenevasen, J.L.M. de Boer and H. Cerfontain, to be published.
3. J. Kelder and H. Cerfontain, Tetrahedron Lett. <u>1972</u>, 1307.
4. J. Kelder and H. Cerfontain, Tetrahedron Lett. <u>1974</u>, 739.
5. J.J.I. Overwater, Thesis (in English), University of Amsterdam, 1969, p. 28.
6. Acetone and biacetyl have been taken as models for AH and DK respectively.
7. J.C. Dalton and N.J. Turro, Ann. Rev. Phys. Chem. <u>21</u>, 499 (1970).
8. N.J. Turro, "Molecular Photochemistry", Benjamin, New York, 1967.
9. S.L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, p. 55.
10. C.H.J. Wells, "Introduction to Molecular Photochemistry", Chapman and Hall, 1972, p. 36; J.G. Calvert and J.N. Pitts Jr., "Photochemistry", Wiley, New York, 1968, p. 301.
11. S.W. Benson, "The Foundation of Chemical Kinetics", McGraw-Hill, New York, 1960, p. 496.
12. k_{isc} (biacetyl) = 8×10^7 s^{-1}, L.G. Anderson and C.S. Parmenter, J. Chem. Phys. <u>52</u>, 466 (1970).