PHOTOCHEMISTRY OF DIENONES-X¹

PHOTOCHEMISTRY OF (E)- β -IONONE OXIME ETHYL ETHER

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Abstract—(E)- β -ionone oxime ethyl ether [(E, E)-4] upon direct irradiation with λ either 254 or 313 nm yields the geometrical isomer (E, Z)-4 and (Z)-retro- γ -ionone oxime ethyl ether (Z, E)-5 as the sole primary products, illustrating (E)-(Z) isomerization $(\phi_{313} = 0.49)$ and a 1, 5-hydrogen shift $(\phi_{313} = 0.15)$ respectively. From studies with triplet photosensitizers and with ethyl iodide (to enhance the singlet-triplet intersystem crossing) it is concluded that these two products in the direct irradiation result only from the singlet excited state, and that the inter-system crossing quantum yield is relatively low. Upon prolonged irradiation of (E, E)-4 with λ 313 nm the eventual products are (Z, E)-5 and (Z, Z)-5, whereas with λ 254 nm they are (E, E)-5 and [(Z, E)-5 and/or (E, Z)-5].

Upon triplet photosensitization (E, E)-4 undergoes only (E)-(Z) isomerization, leading to a mixture of all the four geometrical isomers of 4. From the dependence of the geometrical isomer distribution in the photostationary state on the triplet energy of the sensitizer the triplet energies of (E, E)-4, (E, Z)-4, (Z, E)-4, and (Z, Z)-4 have been determined to be *ca* 55, < 55, 57, and 57 kcal/mol respectively.

The photochemistry of (E)- β -ionone (E)-1 was the subject of various studies.² The direct irradiation yields the isomeric α -pyran 2 and (Z)-retro- γ -ionone 3, whereas the triplet sensitized irradiation gives only 2.^{2c} In view of our interest in the photochemistry of the oxime chromophore,³ it was thought of interest to study the

photochemistry of the oxime ethyl ethers of the ionones. In this paper we report on the direct irradiation of the oxime ethyl ether of 1 with and without added "heavy-atom" solvent,⁴ and on its triplet sensitized irradiation using a variety of photosensitizers.



RESULTS

Direct irradiation of (E, E)-4 and (E, Z)-4. The oxime ether (E, E)-4 in benzene as a solvent upon λ 313 nm irradiation yielded (E, Z)-4, (Z, E)-5, (Z, Z)-4 and (Z, Z)-5 (Fig. 1). The latter two products—in contrast to the former two—are secondary ones, as their formation from (E, E)-4 shows an induction period. The λ 313 nm quantum yields for the formation of the primary products (E, Z)-4 and (Z, E)-5 have been determined as the zero



Fig. 1. Dependence of the product formation on the irradiation time for the λ 313 nm irradiation of 0.041 mmol of (E, E)-4 in 2 ml of benzene. Δ , (E, Z)-4; Δ , (Z, E)-5; \bigcirc , (Z, Z)-4; +, (Z, Z)-5.

conversion limiting value of low (E, E)-4 conversion experiments to be 0.49 and 0.15 respectively.

The direct λ 313 nm irradiation of (E, Z)-4 yielded (E, E)-4, (Z, Z)-4 and (Z, Z)-5 as primary photoproducts (Fig. 2). Upon prolonged irradiation of (E, E)-4, the (E, Z)-4 and (Z, Z)-4 produced are photoconverted again to yield (Z, E)-5 and (Z, Z)-5 as the only final isomeric photoproducts (Fig. 3).



Fig. 2. Dependence of the product formation on the irradiation time for the λ 313 nm irradiation of 0.023 mmol of (E, Z)-4 in 2 ml of benzene. \Box , (E, E)-4; \bigcirc , (Z, Z)-4; +, (Z, Z)-5.



Fig. 3. Dependence of the product formation on the irradiation time for the λ 313 nm irradiation of 0.038 mmol of a 91:9 mixture of (E, E)-4 and (E, Z)-4 in 2 ml of ethanol. \Box , (E, E)-4; \triangle , (E, Z)-4; \triangle , (Z, E)-5; +, (A, Z)-5; \bigcirc , (Z, Z)-4.



Fig. 4. Dependence of the product formation on the irradiation time for the λ 254 nm irradiation of 0.038 mmol of a 53:47 mixture of (E, E)-4 and (E, Z)-4 in 2 ml of ethanol. \Box , (E, E-4; Δ , (E, Z)-4; +, (Z, Z)-5; \odot , [(Z, E)-5 + (E, Z)-5]; \bigcirc , (E, E)-5.

Irradiation of a 53:47 mixture of (E, E)-4 and (E, Z)-4 in ethanol as solvent with λ 254 nm yielded (Z, Z)-5, (Z, E)-5, (E, E)-5 and (E, Z)-5 which has the same glc retention time as (Z, E)-5 (Fig. 4). Upon prolonged irradiation (Z, Z)-5 is again completely photoconverted. The graphs indicate that (E, E)-5 is in any case formed from (Z, Z)-5.

For an irradiation time >4.5 hr the content of the (E, E)-isomer of 5 is constant, viz. $66 \pm 2\%$ which is apparently the photo-stationary state content.

The material balances for the experiments of Figs 3 (λ 313 nm) and 4 (λ 254 nm) and an irradiation time of 9 hr are *circa* 80 and 55% respectively.†

The product formation for the direct irradiation of (E, E)-4 is shown schematically in Scheme 1. The present results do not allow to decide whether the conversion of (Z, Z)-4 into (Z, Z)-5 proceeds via (E, Z)-4 or not.

[†]The lower material balance with λ 254 nm is tentatively ascribed to product formation as result of initial N–O bond homolysis of the electronically excited oxime ethers 4 and 5 which does not occur with λ 313 nm.³⁶

The absence of (Z, E)-4 and 6 among the photoproducts is worth noticing.



Sensitized irradiation of (E, E)-4 and (E, Z)-4. The sensitized irradiation of (E, E)-4 and mixtures of (E, E)-4 and (E, Z)-4 in benzene as solvert has been studied using acridine, 7H-benz[de]-anthracen-7-one, pyrene, fluorenone (in ethanol with some benzene), biacetyl, Michler's ketone, thioxanthone, xanthone (all with λ 403 nm), 4-phenylbenzophenone and benzil (in acetonitril) (the last two with λ 313 nm) as sensitizer. On starting with (E, E)-4 only the other three and on starting with a mixture of (E, E)-4 and (E, Z)-4 only the other two geometric isomers were formed and no retro-y-ionone oxime ethyl ethers 5. Upon prolonged irradiation in the presence of any of these sensitizers a photostationary state (PSS) mixture of all the four geometric isomers of 4 resulted, the composition of which depends on the triplet energy of the sensitizer (Fig. 5). The absence of retro- γ ionone oxime ethyl ethers illustrates that these compounds formed in the direct irradiation of (E, E)-4 and (E, Z)-4 result from the singlet excited states of these substrates.

Direct irradiation of (E, E)-4 and (E, Z)-4 in the presence of ethyl iodide. The effect of added ethyl iodide (which quenches the singlet excited states by enhancing their intersystem crossing efficiencies⁴) on the quantum yields of the product formation for the direct λ 313 nm irradiation of both (E, E)-4 and (E, Z)-4 are shown in Table 1. The data clearly show that the added ethyl iodide affects the quantum yields of the (Z)-4 and (E, Z)-4 are shown in Table 1. The data clearly show that the added ethyl iodide affects the quantum yields of the (E)-(Z) isomerization and the 1, 5-H shift of both (E, E)-4 and (E, Z)-4—yielding (Z, E)-5 and (Z, Z)-5 respectively—to the same extent. The 1, 5-H shift occurs from the singlet excited state of 4 (see before). It is therefore concluded that the (E)-(Z) isomerizations in the direct irradiations also take place exclusively from the singlet excited state.



Fig. 5. Dependence of PSS ratio on the triplet energy of the sensitizer. +, $[(Z, E)-4]/[(E, E)-4]; \bigcirc, [(Z, Z)-4]/[(E, Z)-4]; \bigcirc, [(Z, Z)-4]/[(E, Z)-4]/[(E, Z)-4]; \bigcirc, [(Z, Z)-4]/[(E, Z)-4]/[(E, Z)-4]]; \bigcirc, [(Z, Z)-4]/[(E, Z)-4$

 $[(E, E)-4]/[(E, Z)-4]; \oplus, [(Z, E)-4]/[(Z, Z)-4].$

Table 1. Direct irradiation (λ 313 nm) of (E, E)-4 and (E, Z)-4. Dependence of the relative quantum yields (φ_0/φ	p) on
the concentration of added ethyl iodide	

Reaction		Type of isomerization	4º/4						
			[EtI] mol/l	0.00	0.46	0.50	0.90	1.35	1.67
(<u>E,E</u>)-4 → (<u>E,Z</u>)-4	E → Z		1.00		1.22	1.32	-	1.74
(<u>E,E</u>)-4 → (<u>z.</u> <u>2</u>)-5	1,5-H shift		1.00	-	1.21	1.37	-	1.86
$(\underline{\mathbf{E}},\underline{\mathbf{Z}})-4 \rightarrow (\underline{\mathbf{E}},\underline{\mathbf{Z}})$	<u>E,E)-4</u>	Z → E		1.00	1.06	-	1.20	1.18	-
$(\underline{\mathbf{E}},\underline{\mathbf{Z}})-4 \rightarrow (\underline{\mathbf{E}},\underline{\mathbf{Z}})$	<u>Z,Z</u>)-4	E → Z		1.00	1.10	-	1 .21	1.20	-
$(\underline{\mathbf{E}}, \underline{\mathbf{Z}})$ -4 - (<u>z,z</u>)-5	1,5-H shift		1.00	1.09	-	1.14	1.19	-

DISCUSSION

From the differences in product formation between the direct and the triplet sensitized irradiation of both (E, E)-4 and (E, Z)-4 it is concluded that (Z, E)-5 and (Z, Z)-5 are products resulting from the excited singlet state of (E, E)-4 and (E, Z)-4 respectively by an 1,5-H shift, similarly as 3 is formed from the excited singlet state of (E)-1.^{2c}

The absence of the electrocyclization product 6 for both the direct and the triplet sensitized irradiation of (E, E)-4 and (E, Z)-4 is remarkable. Very recently it was shown that the related ketone (E)-1 upon direct and sensitized irradiation at -50° is first converted into (Z)-1 which upon a subsequent excitation yields the electrocyclization product 2,²⁴ and that on the contrary no electrocyclization products are formed upon irradiation of some trienes in the vitamin A series, except for β -ionylidene acetonitrile.⁵

The photoconversion of (Z, E)-5 and (Z, Z)-5 using λ 254 nm into (E, E)-5 and (E, Z)-5 respectively, proposed in Scheme 1, is analogous to the photochemical formation of (E)-retro- γ -ionone (E)-3 from (Z)-3.⁶ As to the conversion of 4 into 5, the configuration around the C_9 =N bond appears to remain the same.

Upon prolonged irradiation of (E, E)-4 with λ 313 nm the eventual products are (Z, E)-5 and (Z, Z)-5, whereas with λ 254 nm the eventual products are (E, E)-5 and [(Z, E)-5+(E, Z)-5]. The difference is due to the fact that the four *retro*- γ -ionone oxime ethers 5 are electronically excited by irradiation with λ 254 nm, but not with 313 nm.

The photosensitized irradiation of the presently studied substrates 4 leads, as result of a number of photoisomerizations, eventually to a photostationary state (PSS) of all the four geometric isomers. The graphs of the PSS ratios of any two given isomers vs the triplet energy (Fig. 5) may be interpreted in the same way as those for the photoisomerization of simple mono-alkenes⁷ for the following reason. Considering a mixture of the four interconverting geometric isomers of 4, the PSS composition is described by the following set of five equations: The fourth curve, viz. that of $[(Z, E)-4/(Z, Z)-4]_{PSS}$, illustrates that the difference in $E_{\rm T}$ between (Z, E)-4 and (Z, Z)-4 is very small (<2 kcal/mol) in accordance with the estimated values from the other graphs. The triplet energies of the four isomers of 4 are substantially greater than that of (E)-1, 3, 5-hexatriene (47 kcal/mol⁸), close to those of (E)- and (Z)-1, 3-pentadiene (58.8 and 56.9 kcal/mol⁹), (E)- β -ionol (circa 55 kcal/mol¹⁰), and (E)- β -ionone (which is somewhat smaller than 54 kcal/mol¹¹), illustrating that the isomers of 4 behave, just like (E)-1, as dienes. The triplet energy is greater for the C₇=C₈ (Z)- than the (E)-isomers (similarly as the E_T is greater for (Z)- and (E)- β -ionol¹⁰), which is ascribed to the steric interference between the C_5 methyl and the groups at C₉, rendering the C₅-C₆-C₇-C₈ moiety nonplanar.

As to the mechanism of the triplet sensitized interconversion of the four geometric isomers of 4 it is of interest that a *simultaneous* isomerization of two double bonds occurs with (E, E)- and (Z, Z)-2,4-hexadiene¹² and was discussed for some of the geometric isomers of retinal.¹³

The (E)-(Z) isomerization and the 1, 5-H shift of both (E, E)-4 and (E, Z)-4 are affected to the same extent by added ethyl iodide (Table 1). Since the 1,5-H shift takes place from the singlet excited state of (E, E)-4 and (E, Z)-4 (see Results), this infers that the (E)-(Z) isomerization observed on direct irradiation must also take place exclusively from the singlet excited state. This conclusion is further substantiated by the absence of the triplet excited state product (Z, E)-4 in the direct irradiation of (E, E)-4 or (E, Z)-4. Accordingly the quantum yields for intersystem crossing of (E, E)-4 and (E, Z)-4 are close to zero. Similar low intersystem crossing quantum yields $(\varphi < 0.008)$ were found for some simple retinal Schiff bases.¹⁴

Singlet excited (E, E)-4 isomerizes only by rotation around the C₉=N bond, yielding (E, Z)-4, but not around the C₇=C₈ bond, whereas triplet excited (E, E)-4 isomerizes both at the C₇=C₈ and C₉=N bonds, forming (Z, E)-4 and (E, Z)-4 respectively. Similar differences in

$$\begin{split} & [(E, E)-4]k_q^{EE} \cdot a_1^{EE} + [(E, Z)-4]k_q^{EZ} \cdot b_1^{EZ} + [(Z, E)-4]k_q^{ZE} \cdot c_1^{ZE} + [(Z, Z)-4]k_q^{ZZ} \cdot d_1^{ZZ} = 0 \\ & [(E, E)-4]k_q^{EE} \cdot a_2^{EE} + [(E, Z)-4]k_q^{EZ} \cdot b_2^{EZ} + [(Z, E)-4]k_q^{ZE} \cdot c_2^{ZE} + [(Z, Z)-4]k_q^{ZZ} \cdot d_2^{ZZ} = 0 \\ & [(E, E)-4]k_q^{EE} \cdot a_3^{EE} + [(E, Z)-4]k_q^{ZZ} \cdot b_3^{EZ} + [(Z, E)-4]k_q^{ZE} \cdot c_3^{ZE} + [(Z, Z)-4]k_q^{ZZ} \cdot d_3^{ZZ} = 0 \\ & [(E, E)-4]k_q^{EE} \cdot a_4^{EE} + [(E, Z)-4]k_q^{ZZ} \cdot b_4^{EZ} + [(Z, E)-4]k_q^{ZE} \cdot c_4^{ZE} + [(Z, Z)-4]k_q^{ZZ} \cdot d_4^{ZZ} = 0 \\ & [(E, E)-4]k_q^{EE} \cdot a_4^{EE} + [(E, Z)-4]k_q^{ZZ} \cdot b_4^{EZ} + [(Z, E)-4]k_q^{ZE} \cdot c_4^{ZE} + [(Z, Z)-4]k_q^{ZZ} \cdot d_4^{ZZ} = 0 \\ & [(E, E)-4] + [(E, Z)-4] + [(Z, E)-4] + [(Z, Z)-4] = \text{constant}. \end{split}$$

The first four equations differ only in (the values for) a_i^{EE} , b_i^{EZ} , c_i^{ZB} and d_i^{ZZ} (i = 1, 2, 3, 4), which are functions of the rate constants for decay of the given triplet excited isomers (indicated as superscripts) to the four isomers. The k_q 's denote the rate constants for triplet energy transfer from the sensitizers to the substrate, indicated by the superscript. From these five equations it follows that the [(E, E-4)]((E, Z)-4] ratio in the PSS depends on $k_q^{\text{EZ}}/k_q^{\text{EE}}$, but not on either k_q^{ZE} or k_q^{ZZ} . Similar conclusions are valid for the ratios of the concentrations of any other pair of isomers in the PSS.

Applying the standard interpretation,⁷ it then follows from the three pronounced bell shaped curves that the triplet energies of (E, E)-, (Z, E)- and (Z, Z)-4 will be *circa* 55, 57 and 57 kcal/mol respectively and that the $E_{\rm T}$ of (E, Z)-4 will be somewhat less than that of (E, E)-4. the photochemical (E)-(Z) isomerizations from the S₁ and T₁ state were reported by Liu for some trienes in the vitamin A series,¹¹ e.g. singlet excited β -ionylidene acetone isomerizes only around C₇=C₈, whereas the triplet excited species does only so around C₉=C₁₀.

EXPERIMENTAL

Materials. (E)- β -ionone was converted into its oxime by the method of Büchi and Vederas.¹³ A mixture of 19.3 g oxime, 16.5 ml diethyl sulphate, and 11.3 g NaOH in 43 ml water was stirred at 80° for 30 min. The usual work-up procedure by extraction with ether gave 17.3 g crude oxime ether which after distillation afforded a 53:47 mixture of (E, E)-4 and (E, Z)-4 (bp. 82-91°).0.2 mm) in a yield of 10 g (45%). (E, E)-4 and (E, Z)-4 were separated by means of glc (120 × 1/4 in. copper column, 10% SE-30 on Chromosorb WAW 80-100 mesh).

Irradiations. The direct and sensitized irradiations with λ 313 nm were carried out in pyrex vessels using a Rayonet RPR 206 photochemical reactor equipped with eight RUL 3000 Å lamps, using benzene or EtOH as solvent. The direct irradiations with λ 254 nm were performed in quartz vessels with a Rayonet RPR 204 photochemical reactor equipped with four RUL 2537 Å lamps. The sensitized irradiations with λ 403 nm were carried out using a Philips SP 500 lamp with a λ 403 nm cut-off filter. In all cases the sensitizer was present in such a concentration that is absorbed >98% of the irradiation.

The irradiated mixtures were analysed by glc on a $120 \times 1/8$ in. stainless steel column loaded with 15% SE-30 on Chromosorb WHP 100-120 mesh. The compositions of the irradiated mixtures were determined using $C_{14}H_{30}$, $C_{15}H_{32}$ and $C_{16}H_{34}$ as internal glc standards by use of a Varian CDS 111C digital integrator. The quantum yields were determined by valerophenone actinometry,¹⁶ as described before.¹⁷

Structural assignment. The structural assignment of the various geometric isomers 4 and 5, obtained pure by preparative glc on the columns described before, was based on a comparison of their ¹H NMR spectra with those of the parent ketones (E)-1 and (Z)-3.^{2c} The assignment of the configuration around the C=N bond was made on the basis of the chemical shifts of the hydrogens at C(8), as it was established for a series of α -keto oxime ethers that the hydrogens at the C atom adjacent to the oxime sp² carbon absorb at higher field for the (E)- than for the (Z)-isomer of the oxime ether.³ The H-C(8) of (E, E)-4, (E, Z)-4, (Z, E)-4, and (Z, Z)-4 was found to absorb at 86.11, 7.16, 6.36 and 6.81 ppm respectively, and that of (E, E)-5, (E, Z)-5, (Z, E)-5, and (Z, Z)-5 at 3.13, 3.30, 3.01 and 3.20 ppm respectively.

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