PHOTOCHEMISTRY OF DIENONES—VIII¹

THE LOW TEMPERATURE PHOTOCHEMISTRY OF (Z)- β -IONONE AND ITS PHOTO-ISOMERS

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Abstract—The isomerizations of (E)- β -ionone 1, and of mixtures of the isomeric pyran 2 and (Z)- β -ionone 3 in CD₃OD as solvent on direct irradiation with λ 254 nm and on triplet photo-sensitization have been studied at temperatures $\leq -50^\circ$, where the thermal isomerization between 2 and 3 is fully inhibited. The *direct* irradiation of 1 at -60° leads to 3 and (Z)-retro- γ -ionone 4 as primary products; 3 is subsequently rapidly photo-converted into mainly 2. Evidence is presented that 4 is also a primary photoproduct from both 2 and 3. The quantum yield ratio $\phi_{2-4}: \phi_{3-4} \approx 0.50$. On starting with either 1 or mixtures of 2 and 3 the same photo-stationary equilibrium ratio of 1-3 is eventually obtained, viz 1:2:3 \approx 17:72:11. 4 is photostable relative to 1-3.

The perdeuterobenzophenone *triplet photo-sensitization* with λ 366 nm at -50° of 1 leads to 3 as the sole primary product, which isomer on triplet sensitization yeilds both 1 and 2. The triplet sensitized conversion is much faster for (Z)- than (E)- β -ionone. On starting with either 1 or mixtures of 2 and 3, eventually the same photo-stationary state is obtained, viz 1:2:3 \approx 39:46:15. (Z)-retro- γ -ionone 4 is not formed in the triplet sensitized irradiations of 1, 2 and 3 and in the direct irradiation it apparently results from the singlet excited state of the three substrates.

The UV spectrum of the (unstable) (Z)- β -ionone 3 has been indirectly determined; its absorption occurs at lower wavelength and is of lower intensity than that of the (*E*)-isomer 1.

It was proposed by various investigators that the photoisomerization of (E)- β -ionone 1 into the isomeric α pyran derivative 2 proceeds via (Z)- β -ionone 3 as intermediate,¹⁻⁴ although no direct evidence for the occurrence of 3 as intermediate was presented. Relevant for the proposal is, however, Marvell's observation that heating of a solution of the α -pyran derivative 2 in, e.g. tetrachloroethene at 120° yields (Z)- β -ionone 3. In fact 2 and 3 are in a strongly temperature dependent equilibrium.⁵

Upon direct irradiation of 1 and also 2 some (Z)-retroy-ionone 4 is formed as a primary photoproduct which was shown to result from an excited singlet state.¹⁴

Compound sheet



In order to obtain information as to the intermediacy of (Z)- β -ionone 3 in the photo-interconversion of 1 and 2, the photoreactions and the analyses of the resulting mixtures have now both been performed at low temperatures in order to prevent the thermal conversion of 3 into the α -pyran 2.

RESULTS

Equilbrium compositions and UV spectra of 2 and 3. The equilibrium compositions of mixtures of 2 and 3 at a given temperature, obtained on dissolving the α -pyran 2 in the appropriate solvent and heating the solution at that temperature for 15 min, are listed in Table 1. 2 and 3 in CD₃OD as solvent at $\leq -50^{\circ}$ do not interconvert, as the non-equilibrium isomeric composition of mixtures of 2 and 3 did not vary over a period of 12 hr.

The UV absorption spectrum of (Z)- β -ionone (3) and the α -pyran 2, determined by a two component analysis on mixtures of 2 and 3, are shown in Fig. 1, together with that of their photo-isomer 1.

Direct irradiations. The results of the direct irradiations of 1 and of mixtures of 2 and 3 with λ 254 nm at -60° are shown in Fig. 2. The material balances after 10 hr irradiation were ca 95%. Irradiation of 1 leads to (Z)- β -ionone 3 and (Z)-retro- γ -ionone 4 as the primary products. The amount of 3 levels off after 3 hr irradiation. 3 is apparently photo-converted into the α -pyran derivative 2, the formation of which does show an induction period (see Fig. 2A). The eventual ratio of $1:2:3 \approx 16:72:12$. The same equilibrium ratio is obtained on starting with a 84:16 mixture of 2 and 3 (Fig. 2B).

The initial increase in the α -pyran 2 at the cost of (Z)- β -ionone 3 is much more pronounced on starting with the mixture of 2 and 3 which is richer in 3 (see Figs. 2B and 2C).

The initial rate of formation of (Z)-retro- γ -ionone 4 in the direct irradiation is the same on starting with a 81:19 and a 64:36 mixture of 2 and 3 (Fig. 3). Figure 3 further illustrates that 4 is a primary photo-product. 4 is photostable in comparison with 1-3.

Triplet photo-sensitization. The results of the perdeuterobenzophenone triplet photo-sensitized reactions

Solvent	Temp. (°C)	Composition (%)		Ref.
		Ş	3	
$cl_2 c = ccl_2$	18	91	8.6	5
	31	91 <u>+</u> 1	9 <u>+</u> 1	
	54	82	17.8	5
	58	83 <u>+</u> 1	17 <u>+</u> 1	
	108	70+2	30 <u>+</u> 2	
	113	60	40 [–]	5
CD ₂ CN	20	85 <u>+</u> 1	15 <u>+</u> 1	
,	58	73±2	27 <u>+</u> 2	
	73	60 <u>+</u> 2	40 <u>+</u> 2	
CD ₃ OD	18	81 <u>+</u> 1	19 <u>+</u> 1	
	31	75 <u>+</u> 2	25 +2	
	60	61 <u>+</u> 2		
c _{6^D5^{CD}3}	105	72 <u>+</u> 2	28 <u>+</u> 2	

Table 1. Equilibrium compositions^a of the α -pyran derivative 2 and (Z)- β -ionone 3^b

^a The variation in the 2 : 3 ratio with temperature is reversible.

^b On heating of the α -pyran in DMSO at 148°C for 15 min 25% of 4 was formed irreversibly in addition to 50% of 3 and 25% of 2.



Fig. 1. UV absorption spectra, solvent Mech; 1 ---- $\lambda_{max} = 291 \text{ nm}$, $\epsilon = 96001./\text{mol} \cdot \text{cm}$; 2 ---- $\lambda_{max} = 285 \text{ nm}$, $\epsilon = 47501./\text{mol} \cdot \text{cm}$; 3 ···· $\lambda_{max} = 285 \text{ nm}$, $\epsilon = 13501./\text{mol} \cdot \text{cm}$.

of 1 and mixtures of 2 and 3 at -50° using λ 366 nm are shown in Fig. 4.

The upper limit of (Z)-retro- γ -ionone was estimated from the absence of its specific ¹H NMR vinyl hydrogen absorptions to be 1%. The material balances after 12 hr irradiation were ca 85%. Starting with (E)- β -ionone as substrate (Fig. 4A), the initial product is (Z)- β -ionone, whereas the α -pyran 2 is formed only by a subsequent photo-sensitization of (Z)- β -ionone. Figure 4C illustrates that (Z)- β -ionone upon photo-sensitization yields directly (E)- β -ionone. From a comparison of the Figs. 4A and 4C it follows that the triplet photo-sensitized conversion is much slower for (E)- and (Z)- β -ionone. For long irradiation times an equilibrium ratio of $1:2:3 \approx$ 39:46:15 is obtained (Figs. 4A and 4B).

DISCUSSION

The UV absorption of (Z)- β -ionone is at lower wavelength and of lower intensity than that of (E)- β ionone, indicating that there is less conjugation in the



Fig. 2. Direct irradiation in CD₃OD at -60° with λ 254 nm of 1 (A) and mixtures of 2 and 3 of different compositions; 81:19 (B) and 64:36 (C). ○, — 1; □, — 2; △, ---3; +, — 4.



Fig. 3. Formation of retro- γ -ionone in the direct irradiation (λ 254 nm) in CD₃OD at - 50° on starting with a 81:19 (O) and 64:36 (+) mixture of 2 and 3.

former compound. A study of the Stewart molecular models reveals that the side chain of (Z)- β -ionone is out of the plane of the cyclohexenyl carbons of the CMe₂-CR=CMe-CH₂ moiety, as result of steric repulsion by the geminal dimethyls and the ring sp² bonded Me,† whereas with (E)- β -ionone this is far less so. The model of (Z)- β -ionone further showed that the single(Z) conformation of the C₈-C₉ single bond is preferred over the single-(E) one.



The present results on the direct and photo-sensitized irradiations have revealed that 4 is an excited singlet state product from each of the three substrates 1-3, formed by a signatropic 1,5-H shift, as shown in Scheme I. A careful examination of framework molecular models (Dreiding and Prentice Hall) showed that also with the α -pyran 2 one of the Me hydrogens is located in a favourable position to migrate to C₈.

The initial rate of formation of (Z)-retro- γ -ionone 4 is the same on 254 nm irradiation of a 81:19 and a 64:36 mixture of 2 and 3. Thus, by coincidence $\epsilon_2 \cdot \phi_{2 \to 4} \approx \epsilon_3 \cdot \phi_{3 \to 4}$. For λ 254 nm $\epsilon_2 = 1500$ and $\epsilon_3 = 7501./mol \cdot cm$ (see Fig. 1) and accordingly $\phi_{2 \to 4}/\phi_{3 \to 4} \approx 0.50$. This value may reflect a more constrained transition state for the conversion of the singlet excited state of 2 than of 3 into 4, possibly because of the bicyclic structure of 2 (see Scheme 1).

The triplet photosensitized conversion is much slower for (E)- than (Z)- β -ionone. This infers, provided that the rate of triplet energy transfer to both isomers is the same (see later), that the chemical reactivity is smaller for triplet excited (E)- than (Z)- β -ionone.

Comparison of the direct with the triplet sensitized irradiations. In the initial stages of the irradiation of the 64:36 mixture of 2 and 3 there is an increase in the amount of the α -pyran 2 for the direct irradiation, whereas for the triplet photo-sensitized one there is not (see Figs. 2C and 4C). Considering the triplet energy transfer from triplet excited benzophenone to each of the three compounds to be diffusion controlled,[‡] the ratio in which the triplet excited states of 1, 2 and 3 are formed in the very beginning will be equal to the ratio of the starting concentrations of these compounds, i.e. during irradiation the corresponding singlet excited states formed in the beginning will be equal to the ratio of the

[†]The π - π^* absorption of (Z)- β -ionone is at much higher wavelength than that of a simple α , β -enone ($\lambda_{max} = 285 \text{ vs } 224$ -249 nm⁶). This indicates that there still exists some conjugation between the cyclohexenyl double bond and the side chain.

[‡]This presumption is met for 1 and 2, as their triplet energies are smaller than that of benzophenone, viz. <54 and $54-56^{\circ}$ vs 68.5 kcal/mole.⁷ The triplet energy of 3 is not reported. Its UV absorption is in between that of an $\alpha_{*}\beta$ -enone and an $\alpha_{*}\beta_{-7}$,8dienone (Results). Its triplet energy may therefore be in between 69 and <54 kcal/mol (the triplet energy values for propenal⁸ and 1' respectively) which is then also smaller than that of benzophenone.



Fig. 4. Perdeuterobenzophenone triplet sensitized irradiation in CD₃OD at -50° with λ 366 nm of 1 (A) and mixtures of 2 and 3 of different compositions; 85:15 (B) and 59:41 (C). ○, — 1; □, — 2; △, ---3.

products of the initial concentrations of the compounds and their molar extinction coefficients, i.e. $0:(64 \times 1560):(36 \times 740) = 0:79:21$. The initial increase of the α -pyran 2 in the direct irradiation (Fig. 2C) which is absent in the triplet photo-sensitized isomerization (Fig. 4C) may then in view of the higher ratio of excited 2 over excited 3 in the direct as compared with the triplet sensitized irradiation be explained (i) in terms of a very low rate of both the chemical conversion and intersystem crossing of the singlet excited state of 2 and (ii) in terms of formation of the α -pyran 2 from the singlet excited state of 3. The more rapid initial decrease of 3, despite the lower degree of excitation of 3, for the direct (Fig. 2C) as compared with the triplet sensitized (Fig. 4C) irradiation, is in line with the second explanation.

The very low rate of chemical reactivity and i.s.c. of singlet excited 2 also follows from a comparison of the p.s.s. ratios of the interconverting species 1-3 for the direct and triplet sensitized irradiation, considering that the ratio of excited species 1:2:3 in the p.s.s. for the direct irradiation is $(16 \times 970):(72 \times 1560):(12 \times 970) =$ 11:81:8 and for the triplet sensitized irradiation 39:46:15.

In conclusion it appears that (i) (Z)- β -ionone upon triplet sensitization at -50° is converted into both (E)- β ionone and the α -pyran 2, (ii) the photo-sensitized conversion is slower for (E)- than (Z)- β -ionone, (iii) the α -pyran 2, resulting both in the direct and the triplet sensitized irradiation of (E)- β -ionone as starting substrate, is a secondary product formed by excitation of the primary product (Z)- β -ionone, and (iv) the chemical reactivity of singlet excited 2 is relatively low.

EXPERIMENTAL

(E)- β -ionone was obtained as a gift from Naarden International, Holland. The isometric α -pyran 2 was obtained by irradiation of $(E) - \beta$ -ionone (10 g) in EtOH (500 ml) at 10° with λ 254 nm and purified twice by repeated silicagel column (1= 0.85 m, $\phi = 4$ cm) chromatography, using a 9:1 (v/v) mixture of P.E. 60-80 and EtOAc as eluent; yield 4g. Perdeuterobenzophenone was obtained from Merck, Sharp & Dohme (Montreal).

The low temp mixtures of 2 and 3 in the solvent of choice were

obtained by heating ca 60 or 33 mg of 2 in 0.5 ml of the solvent, contained in a quartz ¹H NMR tube at the desired temp (see Table 1) for 15 min. Immediately thereafter the mixture was frozen in liquid N₂ for 5 min and then transferred to a dry ice-EtOH bath kept at -70° in which they were kept until ready to use.

Direct irradiations. The irradiations were performed in a silver coated Dewar vessel containing EtOH (free of aromatics) in which a merry go round, a low pressure U-shaped Hanovia 4 W PCR 11 immersion lamp (yielding mainly λ 254 nm) and a cooling spiral were placed. The low temp in the Dewar was attained by circulating MeOH from an Ultra-Kryomat (Lauda K 75 DW) through the cooling spiral. Solns of 1 (60 mg) in CD₃OD (0.5 ml) or the chilled ready to use solns of mixtures of 2 and 3 (total 60 mg) (see just before), each containing a drop of TMS and a known amount of nitromethane (internal ¹H NMR standard) in quartz ¹H NMR tubes were then placed in the Dewar and, after 20 min of temp adjustments, irradiated for the desired length of time.

Photosensitized irradiations. These irradiations were performed in a Rayonet RPR-208 photochemical reactor equipped with eight λ 366 nm lamps in which centre a transparant pyrex Dewar vessel was placed. This vessel contained MeOH kept at -50° as described for the direct irradiations. The pyrex ¹H NMR tubes containing solns of 1 (33 mg) in CD₃OD (0.5 ml) or the chilled ready to use solns of mixtures of 2 and 3 (total 33 mg), each containing perdeuterobenzophenone (0.37 M), a drop of TMS, and a known amount of nitromethane, were placed in a concentric array in the Dewar. After 20 min for temp adjustment, the solns were irradiated for the desired length of time.

Analysis of mixtures of 2 and 3. The compositions of the mixtures of 2 and 3 in the solvent of choice at a given temp $\geq 20^{\circ}$ after an equilibration period of 20 min was determined at that temp by two component ¹H NMR analysis on the basis of the specific vinylic hydrogen absorptions of 2 and 3 (Table 2). The composition of the frozen low temp mixtures of 2 and 3 were analyzed directly at that low temp in a similar fashion.

Analysis of the irradiated reaction mixtures. The composition of the irradiated solns was determined by multicomponent analysis from the ¹H NMR spectra (see Ref. 9) recorded from these solns directly at -60 or -50° on the basis of the specific vinylic hydrogen absorptions of the various components (Table 2), using nitromethane as internal standard.

UV spectra. The individual absorption spectra of 2 and 3 were determined from the spectra of the solns made up from the α -pyran in acetonitrile which were recorded after an equili-

Table 2. Vinylic ¹H NMR absorptions in CD₃OD at -60°

	CHCH _n (CO)Me ^a	C <u>H</u> (CO)Me	>сн ₂
1	7.35(d;16)	6.05(d;16)	
2	5.60(d;6)	4.94(a;6)	
3	6.65(d;12)	6.07(d;12)	
4	5.34(t;7)		4.9 ⁵ (m);4.45(d;2.5)

Compound Chemical shifts (p.p.m.), multiplicities, and coupling constants (Hz)

^a For
$$1 - 3n = 1$$
 and for $4n = 2$.

bration period of 15 min at 20 and 73°. For a given wavelength λ_{i} , considering the molar extinction coefficients at 20 and 73° to be the same,† the extinctions are given by

$${}^{20}E_{\lambda_1}E = {}_{\lambda_1}\epsilon_2 \cdot {}^{20}c_2 + {}_{\lambda_1}\epsilon_3 \cdot {}^{20}c_3 \qquad (1)$$

$${}^{73}_{\lambda_1} \mathbf{E} = {}_{\lambda_1} \epsilon_2 \cdot {}^{73} c_2 + {}_{\lambda_1} \epsilon_3 \cdot {}^{73} c_3 \tag{2}$$

in which the subscripts 2 and 3 refer to the respective compounds. The concentrations of 2 and 3 at the two temps were calculated from the total initial substrate concentration and the $c_2:c_3$ ratio reported in Table 1.‡ For each wavelength ϵ_2 and ϵ_3 were then calculated from the thus determined concentrations and the measured extinctions using the Eqs (1) and (2).

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[†]This was in fact observed for (E)- β -ionone.

^{*}This treatment infers that the $c_2: c_3$ ratio is independent of the total substrate concentration in between 0.0002 M (UV concentration) and 0.62 M (¹H NMR concentration), as may be expected for the unimolecular equilibration of the α -pyran (2) and (Z)- β -ionone.⁵