UVA Self-Photosensitized Oxygenation of β -lonone

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ABSTRACT

The steady-state UVA (350 nm) photolysis of (*E*)- β -ionone (1) in aerated toluene solutions was studied by ¹H NMR spectroscopy. The formation of the 1,2,4-trioxane (2) and 5,8-endoperoxide (5) derivatives in the ratio of 4:1 was observed. Time-resolved laser induced experiments at 355 nm, such as laser-flash photolysis, photoacoustic and singlet oxygen ¹O₂ phosphorescence detection, confirmed the formation of the excited triplet state of 1 with a quantum yield $\Phi_{\rm T} = 0.50$ as the precursor for the generation of singlet oxygen ¹O₂ ($\Phi_{\Delta} = 0.16$) and the isomeric α -pyran derivative (3), which was a reaction intermediate detected by NMR. In turn, the reaction of ¹O₂ with 1 and 3 occurred with rate constants of 1.0×10^6 and 2.5×10^8 m⁻¹s⁻¹ to yield the oxygenated products 5 and 2, respectively, indicating the relevance of the fixed *s-cis* configuration in the α -pyran ring in the concerted [2 + 4] cycloaddition of ¹O₂.

INTRODUCTION

The reaction of singlet molecular oxygen ${}^{1}O_{2}$ with olefinic compounds is one of the general photochemical oxidations (1). These processes, classified as Type II photooxygenations, are highly selective showing often the characteristics of pericyclic pathways. Depending on the nature of the olefinic target, valuable intermediates such as allylic hydroperoxides, endoperoxides (1,2-dioxenes) and 1,2-dioxetanes result from the reactions involving ${}^{1}O_{2}$ via three principal classes—*ene* reaction, [2+2] and [2+4] cycloadditions (2,3). These transformations represent powerful protocols for introducing molecular oxygen in a highly specific fashion into organic compounds with wide applications in organic synthesis (2–4).

Usually, ${}^{1}O_{2}$ is generated by an energy-transfer mechanism after photoexcitation of a sensitizer dye molecule in the presence of ground-state triplet oxygen, ${}^{3}O_{2}$ (1–4). The reaction of ${}^{1}O_{2}$ with the singlet ground state of organic molecules is so specialized that examples of spontaneous addition of ${}^{3}O_{2}$ are rare. However, certain types of olefinic compounds undergo light-induced oxidation without dye sensitizer, and in those cases self-photosensitized oxygenation mechanisms have been proposed to rationalize the formation of the oxygenated products (5,6). (*E*)- β -ionone (1) is a natural short-chain analog of the polyenes retinoid and carotenoids, hence studies on its phototransformations have attracted considerable attention (7,8). In addition, ionones and their derivatives are highly valued fragrance constituents and important building blocks in organic synthesis (9–11). In this context, in previous work we reported that UVA (350 nm) irradiation of 1 under aerobic conditions resulted in the formation of the 1,2,4-trioxane derivative 2, which is a 6-member heterocycle containing three oxygen atoms (Scheme 1) (12,13). To the best of our knowledge it was the first report on the spontaneous light-induced addition of O₂ in the ionone series without the presence of a dye-sensitizer molecule, uncovering a new aspect in the area of the ionone photochemistry.

On the basis of these previous reports, in this work we present a kinetic study of the UVA-photoinduced transformation of **1** in aerated toluene solutions monitored by ¹H NMR spectroscopy, and also by performing time-resolved laser-induced experiments, such as transient absorption and photo-acoustic spectroscopies, and NIR phosphorescence detection of ¹O₂.

MATERIALS AND METHODS

(E)- β -ionone (1), 2-hydroxybenzophenone (HBP), 1,4-diazabicyclo[2.2.2]octane (DABCO) and perinaphthenone (PN) were from Sigma (St. Louis, MO), 9,10-dimethylanthracene (DMA) was from Aldrich (Milwaukee, WI). High purity argon was from Indura (Tucuman, Argentina). Toluene (HPLC grade) was from Sintorgan (Buenos Aires, Argentina). All chemicals were used as supplied.

Typically, a 10 mm 1 toluene solution was placed in a Pyrex vessel (cutoff at 310 nm) and irradiated under aerobic conditions at room temperature in a Rayonet RPR 100 photochemical reactor with a





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RPR-3500 UVA lamp (maximum output at 350 nm). The ¹H spectra were recorded at 300 and 75 MHz on a Bruker AVANCE NMR spectrometer in CDCl₃ solutions. Chemical shifts are given in δ using Me₄Si as internal standard (12,13). The resonance signals of the components of the reaction mixture were well separated in the olefinic region allowing their analysis by ¹H-NMR spectroscopy. Periodically a 10 mL aliquot of the reaction mixture was removed, and after evaporation of the solvent, the crude materials were used to record the NMR spectra. The component distribution was estimated by the integration of the NMR peaks of the starting substrate and the products in the vinylic region (4.5–7.5 p.p.m.).

UV-Vis absorption and fluorescence spectra of 1 were recorded with an HP 8453 photodiode array spectrophotometer and a Hitachi F-2500 spectrofluorometer, respectively. All time-resolved laserinduced experiments were performed with an Nd-YAG laser (Continuum Minilite II) as excitation source generating 355 nm pulses of 5 mJ and 10 ns pulse width. Transient absorption spectra were recorded with a Luzchem m-LFP 112 laser-flash photolysis system. Time-resolved photoacoustic experiments were completed with a home-made system with an acoustic transit time of 500 ns as described before (14,15). To avoid degradation of the sample less than 10 single laser shots of $< 100 \ \mu$ J were averaged. The calorimetric reference HBP was used and the absorbance at 355 nm of both reference and sample solutions was matched within $\pm 2\%$. Time-resolved phosphorescence detection of ${}^{1}O_{2}$ was done using a home-made system (16), composed of a Peltier cooled Ge photodiode (Judson J16TE2-66 G) placed at right angle to the excitation laser pulse. Spurious light was filtered with a 1270 nm band pass filter (Spectrogon BP-1260). In all cases, the transient signals were fed to a Tektronix TDS3032B digital oscilloscope linked to an on-line PC for data transfer and analysis. The experiments were performed in duplicate under controlled temperature of 25 $\pm 1^{\circ}$ C.

RESULTS AND DISCUSSION

Photo-stationary experiments

Figure 1 shows the ¹H NMR spectrum after 60 min of UVA irradiation of **1** in toluene solutions under aerobic conditions. Because of their typical vinylic hydrogen resonances (12,13), the formation of **2** with two doublets at δ 6.42 and 6.53 p.p.m. (J = 8.5 Hz) and the presence of **1** with two doublets at 6.11 and 7.27 p.p.m. (J = 16.4 Hz) was assigned. In addition, the doublets attributed to α -pyran **3** were found at 5.02 and



Figure 1. ¹H NMR spectrum (300 MHz, Cl₃CD) of **1** (10 mM) in airsaturated toluene solution after 60 min of UVA irradiation. Inset: NMR kinetic curves for the components of the reaction mixture: (\blacksquare) **1**, (\Box) **2**, (\bullet) **3** and (\bigcirc) **5**.

5.68 p.p.m. (J = 5.8 Hz). The doublet signals at 4.59 and 5.75 p.p.m. (J = 5.8 Hz) were attributed to endoperoxide 5, according to reported data (17). The inset of Fig. 1 shows the kinetic curves for the photolysis of 1, indicating that the complete depletion of 1 was accompanied by the simultaneous formation of the trioxane 2 (ca 80%) and the endoperoxide 5 (ca 20%). The concentration of the isomeric α -pyran derivative 3 was increased in small proportion at the beginning of the photolysis and afterward depleted, indicating that the α -pyran was a reaction intermediate. The formation of 3 takes place via a hetero-electrocyclization equilibrium from the cis-isomer (Z)- β -ionone 4, which in turn is generated by isomerization from the excited triplet state of 1 (7,18-20). Under our experimental conditions, the cis isomer 4 was not detected in the NMR experiments. This result is expected because of the large shift of the isomerization equilibrium to the formation of 3 from 4 at room temperature ($K \approx 10$ at 18°C) (21). Conversely, the ¹H NMR analysis of the reaction mixture irradiated in toluene solutions saturated with DABCO, a wellknown quencher of ${}^{1}O_{2}$ (22), mainly showed the presence of 1 and 3, indicating the key role of ${}^{1}O_{2}$ on the formation of 2 and 5 (data not shown).

Time-resolved laser-induced experiments

Figure 2 shows the transient absorption spectrum of the triplet state of β -ionone (³1*) obtained by laser-flash photolysis upon excitation at 355 nm of 3 mm 1 in argon-saturated toluene solution. The transient absorption maximum at 335 nm and lifetime of 132 ns for ³1* were similar to those reported in hexane (23) and benzene (24). The triplet quantum yield (Φ_T) of ³1* was determined by time-resolved photoacoustic experiments. Figure 3 shows the photoacoustics for both the calorimetric reference HBP and the sample 1 obtained after 355 nm laser excitation of argon-saturated toluene solutions.

In time-resolved photoacoustic experiments, the observed sample signal S(t), Eq. (1), is the convolution of the instrumental function R(t) (the signal of the calorimetric reference



Figure 2. Transient absorption spectrum of 1 (3 mM) in argonsaturated toluene solutions at different times after the laser pulse at 355 nm. Inset: ${}^{3}1^{*}$ decay signals at 340 nm in argon- and air-saturated toluene solutions.



Figure 3. Laser-induced photoacoustics for the calorimetric reference HBP and sample 1 (1 mM) in argon-saturated toluene solutions, together with the two-sequential exponential fitting simulation (dashed line).

that releases all the absorbed energy as heat) and the sample function H(t), Eq. (2), with φ_i and τ_i as the amplitude factor and lifetime for the *i*-th transient, respectively (25).

$$S(t) = R(t) \otimes H(t) \tag{1}$$

$$H(t) = \sum_{i} \frac{\varphi_{i}}{\tau_{i}} \exp\left(-t / \tau_{i}\right)$$
(2)

Satisfactory fits were obtained with a sum of two exponential decays in the fitting function (dashed line in Fig. 3). The lifetime of the fast component of the acoustic wave was fixed at $\tau_{\text{fast}} \leq 10$ ns because of the duration of the excitation laser pulse. Therefore, this component considers all the relaxation processes involved in the formation of ³1* during the laser pulse, Eq. (3).

$$1 \xrightarrow{h_{\nu}}{1} 1 * \xrightarrow{\Phi_{T}}{3} 1 *$$
(3)

Because the contribution of the structural molecular changes (*i.e.* volume changes, ΔV_{str}) to the acoustic wave in the formation of ³1* is expected to be negligible, as no intramolecular charge transfer or solvent hydrogen bonding interactions occur, the photoacoustic technique behaves as a photocalorimetric method (15,26). Therefore, the fitted amplitude factor for the fast component of the acoustic wave $\varphi_{\text{fast}} = 0.69$ represents the fraction of the laser energy per absorbed photon at 355 nm ($E_{355} = 337$ kJ mol⁻¹) that is released as prompt heat in the formation of ³1*. The measured fluorescence quantum yield of 1 was very low ($<10^{-4}$) and consequently the fraction of the absorbed energy dissipated as light was negligible. Thus, the amount of the energy "stored" during the formation of ³1* is given by Eq. (4), where E_{T} is the energy content of ³1* (=207 kJ mol⁻¹) (23).

$$\Phi_T E_T = E_{355} (1 - \varphi_{\text{fast}}) \tag{4}$$

The $\Phi_{\rm T} = 0.50~(\pm 0.02)$ was calculated from Eq. (4), a value in accord with that obtained by laser-flash photolysis in benzene solutions (24). On the other hand, the slower component φ_{slow} , contains information of the decay of ³1^{*}, as the fitted lifetime of the acoustic signal $\tau_{slow} = 140$ ns was similar to the triplet lifetime obtained by laser-flash photolysis (see above). However, ${}^{3}1^{*}$ is the precursor of the *cis* isomer 4, which in turn is equilibrated with the corresponding heterocyclic isomer 3 (19,21). The lifetime of both forward and reverse isomerization reactions is in the range of hundreds of seconds (21), exceeding by far the upper time resolution of the photoacoustic experiment, i.e. <2 µs. Therefore, it is expected that the slower photoacoustic component $\varphi_{slow} = 0.38$ reflects the ${}^{3}1^{*} \rightarrow 4$ isomerization process in addition to the relaxation process to the ground state of 1. Therefore, it is inaccurate to assume that $\Delta V_{\rm str} \approx 0$ during the decay of ³1*, as isomerization processes in organic solvents are accompanied by important $\Delta V_{\rm str}$ contributions because of solvent reorganization effects (27). Therefore, solvent-dependent protocols or theoretical calculations are needed to separate the heat and structural volume contributions of the acoustic wave (27), procedures that are out of the scope of this report.

As shown in the inset of Fig. 2, in air-equilibrated toluene solutions the lifetime of ³1* was shortened to 64 ns, indicating that the fraction of triplet states quenched by ground state molecular oxygen ${}^{3}O_{2}$, $\eta_{T\Sigma} = [1 - (\tau_{T}{}^{Air}/\tau_{T}{}^{Ar})] = 0.52$. Considering that in air-saturated organic solvents the ${}^{3}O_{2}$ concentration is *ca* 2 mM, a quenching rate constant of *ca* $4 \times 10^{9} \text{ m}^{-1}\text{s}^{-1}$ was calculated, which is a typical value for the quenching of the triplet state of organic molecules by ${}^{3}O_{2}$ (1). The quenching process produces ${}^{1}O_{2}$, as confirmed by the direct detection of the phosphorescence decay signal of ${}^{1}O_{2}$ at 1270 nm after laser excitation of air-saturated toluene solutions of **1** (Fig. 4).

The quantum yield of formation of ${}^{1}O_{2}$, Φ_{Δ} , produced by **1** was determined by extrapolation of the initial intensity (I_{0}) of the ${}^{1}O_{2}$ signal by the first-order fitting of the phosphorescence decay, as the I_{0} value is proportional to Φ_{Δ} , Eq. (5) (28).

$$I_0 = \kappa k_{\rm ph} \Phi_{\Delta} (1 - 10^{-A}) E_l \tag{5}$$

 κ is a proportionality instrumental constant, $k_{\rm ph}$ is the solvent-specific radiative decay rate constant for ${}^{1}O_{2}$, E_{l} is the incident laser energy and A is the absorbance at the excitation wavelength. Thus, the Φ_{Δ} value for 1 can be obtained by simple comparison of the slopes of the linear plot of I_{0} vs E_{l} for the sample and reference compounds under identical experimental conditions. In this case, PN ($\Phi_{\Delta} = 0.92$) was used as reference compound (28). The top inset of Fig. 4 shows the I_{0} vs E_{l} plots



Figure 4. Phosphorescence decay signals of ${}^{1}O_{2}$ at 1270 nm obtained by photosensitization at 355 nm of both the reference PN (50 μ M) and sample **1** (5 mM) in aerated toluene solutions together with the exponential fitting of the decay portion. Top inset: Laser energy dependence of the zero time intensity of the ${}^{1}O_{2}$ signal, I_{0} , Eq. (5). Bottom inset: dependence of the observed decay rate constant of ${}^{1}O_{2}$, k_{Δ} , vs the concentration of **1**, Eq. (9).

obtained for 1 and PN in air-saturated toluene solutions with $A_{355} = 0.7$ in both cases. The linearity of the plots with zero intercepts rules out undesirable phenomena such as multiphotonic absorption or ground state depletion, and the slope comparison allowed the calculation of $\Phi_{\Delta} = 0.16 (\pm 0.02)$ for 1. In addition, Φ_{Δ} is related with all the sequential processes involved in the production of ${}^{1}O_{2}$, Eq. (6).

$$\Phi_{\Delta} = \Phi_T \eta_{T\Sigma} S_{\Delta} \tag{6}$$

 S_{Δ} is the fraction of quenching events that yields free ¹O₂. According to Eq. (6) and the calculated $\eta_{T\Sigma}$ and Φ_{T} values, $S_{\Delta} = 0.62$ was obtained, indicating that *ca* 60% of the quenched ³1* produces ¹O₂.

The lifetime of ${}^{1}O_{2}$ observed upon photosensitization of **1** was shorter and depending on its concentration (3 mM < [**1**] < 9 mM) than that observed for the sensitizer PN (*ca* 50 μ M), with $\tau_{\Delta}^{0} = 27 \ \mu$ s. This indicates the presence of both parallel physical and chemical quenching reactions of ${}^{1}O_{2}$ by **1**, with rate constants $k_{q,1}$ and $k_{r,1}$, respectively, Eqs. (7) and (8).

$${}^{1}\mathrm{O}_{2} + \mathbf{1} \xrightarrow{\mathbf{k}_{\mathbf{q},\mathbf{1}}} {}^{3}\mathrm{O}_{2} + \mathbf{1}$$

$$\tag{7}$$

$${}^{1}\text{O}_{2} + 1 \xrightarrow{\mathbf{k}_{r,1}} \text{Oxidation products}$$
 (8)

The $k_{t,1} = k_{q,1} + k_{r,1}$ is the total rate constant for the whole quenching process of ¹O₂ by **1**, which was obtained by analyzing the observed rate constants for the phosphorescence decay of ¹O₂, k_{Δ} , as a function of the concentration of **1**, Eq. (9),

$$k_{\Delta} = k_{\Delta}^0 + k_{t,1}[\mathbf{1}] \tag{9}$$

 $k_{\Delta}^{0} = (27 \ \mu \text{s})^{-1}$ is the observed decay rate constant of ${}^{1}\text{O}_{2}$ without 1 that was obtained using PN as photosensitizer. The bottom inset of Fig. 4 shows the linear fitting of Eq. (9)



Figure 5. First-order plots for the ${}^{1}O_{2}$ -mediated oxidation of 1, DMA, and 3 in air-saturated toluene solutions. Inset: UV–Vis absorption changes of 3 (every 45 s) produced during the PN-photosensitization at $\lambda > 420$ nm (Schott cutoff filter KV418).

yielding $k_{t,1} = 1.2 \times 10^6 \text{ m}^{-1} \text{s}^{-1}$, indicating that 1 is a modest quencher of ${}^{1}\text{O}_2$ as compared with other related molecules in similar solvents, such as β -carotene ($k_t = 1.1 \times 10^{10} \text{ m}^{-1} \text{s}^{-1}$) (22). This is a consequence of the much higher energy level for the triplet state of 1 ($E_T = 207 \text{ kJ mol}^{-1}$) (23) than for β -carotene ($E_T = 82 \text{ kJ mol}^{-1}$) (29), excluding the possibility to quench ${}^{1}\text{O}_2$ ($E_\Delta = 94.5 \text{ kJ mol}^{-1}$) via a downhill energytransfer mechanism (physical interaction). Consequently the chemical quenching process must be the major component of $k_{t,1}$. In fact, the reactive quenching rate constant of ${}^{1}\text{O}_2$ by 1 was calculated as $k_{r,1} = 1.0 \times 10^6 \text{ m}^{-1} \text{s}^{-1}$ by means of an actinometrical procedure (30), using PN as photosensitizer at > 420 nm and DMA as reference compound, whose reactive quenching rate constant with ${}^{1}\text{O}_2$ is well known, $k_{r,DMA} = 4.7 \times 10^7 \text{ m}^{-1} \text{s}^{-1}$ (22) (Fig. 5).

It is interesting to note that the $k_{r,1}$ value is similar to that obtained for the reaction of ${}^{1}O_{2}$ with β -carotene in AOT reverse micelle solution with rose bengal as photosensitizer (31). In that case, a cyclic 5,8-endoperoxide β -carotene derivative is formed as the primary photooxygenation product by [2+4] cycloaddition of ${}^{1}O_{2}$ (31,32). The formation of 5 is produced by the RB-photosensitized oxygenation of 1 in methanol solutions (17). In addition, the formation of 5,8-endoperoxide derivatives is produced by self-photosensitization of other retinoids, such as retinal (33) and the pyridinium retinoid analog A1E (6). Therefore, on the basis of the above NMR results (Fig. 1) and the reported data for the reaction of ¹O₂ with retinoid-like compounds, the formation of the 5,8-endoperoxide 5 by direct [2+4] cycloaddition reaction of ${}^{1}O_{2}$ to 1, Eq. (8), can be assumed. However, the results of Fig. 1 show that the trioxane 2 was the major photooxidation product (ca 80%). The formation of 2 can be expected by reaction of ${}^{1}O_{2}$ with the α -pyran 3 also by a [2+4] cycloaddition step, Eq. (10), as reported by Etoh et al. in RBphotosensitized reactions in methanol solutions (34).

$$^{1}\mathrm{O}_{2} + 3 \xrightarrow{\kappa_{\mathrm{r},3}} \mathbf{2}$$
 (10)

In our case, the rate constant for reaction (10), $k_{r,3} = 2.5 \times 10^8 \text{ m}^{-1} \text{s}^{-1}$ was obtained by comparison with



Scheme 2. Reaction mechanism proposed for the self-photosensitized oxygenation of (E)- β -ionone.

the actinometer DMA as mentioned before, inset of Fig. 5. The α -pyran **3** was previously formed by 350 nm irradiation of **1** in Ar-saturated solutions, as reported by Büchi and Yang (18). The $k_{r,3}$ value is approximately 1 order of magnitude higher than for 1,3-cyclopentane or 1,3-cyclohexane rings (35), indicating that the electron donating effect of the substituents at the end of the diene unit of **3** could activate the electrophilic attack by ${}^{1}O_{2}$ (3). As compared with **1**, the 250-times higher reactivity of **3** can be assigned to the fixed *s*-cis-1,3-diene configuration of the α -pyran ring, indicating the favorable role played by entropic factors in [2+4] cycloadditions.

CONCLUSIONS

The UVA self-photosensitized oxygenation mechanism of β -ionone in aerated toluene solutions is summarized in Scheme 2. The relevance of this reaction in synthetic routes of stable trioxane precursors, such as 2, is based on the photosensitized formation of ${}^{1}O_{2}$ from 1 and the enhanced reactivity toward ${}^{1}O_{2}$ of the heterocyclic isomer 3, which was also formed by photoisomerization steps from the triplet state of 1. Thus, the reaction sequence for the formation of 2 involves a one-pot three steps domino process (isomerization, hetero-electrocyclization and [2+4] Diels-Alder type oxygen addition) (36), representing an improved procedure for the preparation of 1,2,4-trioxane-type compounds. The formation in less proportion of the 5,8-endoperoxide 5 by direct reaction of 1 with ¹O₂ was also observed, and the relative distribution of oxygenated products [2]/[5] is controlled by the ratio $k_{r,3}[3]/k_{r,1}[1]$.

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REFERENCES

- Turro, N. J. (1978) Modern Molecular Photochemistry. Benjamin/Cummings, Menlo Park, CA.
- Greer, A. (2006) Christopher Foote's discovery of the role of singlet oxygen [¹O₂(¹Δ_g)] in photosensitized oxidation reactions. *Acc. Chem. Res.* **39**, 797–804.

- Clennan, E. L. and A. Pace (2005) Advances in singlet oxygen chemistry. *Tetrahedron* 61, 6665–6691.
- Bartoschek, A., T. T. El-Idreesy, A. G. Griesbeck, L.-O. Höinck, J. Lex, C. Miara and J. M. Neudörfl (2005) A family of new 1,2,4trioxanes by photooxygenation of allylic alcohols in sensitizerdoped polymers and secondary reactions. *Synthesis* 14, 2433–2444.
- Hakimelahi, G. H., M. L. Jain, T. Wei Ly, I.-C. Chen, K. S. Ethiraj, J. R. Hwu and A. A. Moshfegh (2001) Self-sensitized photooxygenation of 3,4-dialkoxyfurans to vitamin C or its derivatives. J. Org. Chem. 66, 7067–7071.
- Jochkush, S., R. X. Ren, Y. P. Jang, Y. Itagaki, H. R. Vollmer-Snarr, J. R. Sparrow, K. Nakanishi and N. J. Turro (2004) Photochemistry of A1E. A retinoid with a pyridinium moiety: Competition between pericyclic photooxygenation and pericyclization. *J. Am. Chem. Soc.* 126, 4646–4652.
- 7. Polyakov, N. E., A. I. Kruppa, V. S. Bashurova, R. N. Musin, T. V. Leshina and L. D. Kispert (1999) Single electron transfer in the phototransformations of β -ionone in the presence of electron acceptor. *J. Photochem. Photobiol. A, Chem.* **128**, 65–74.
- Polyakov, N. E., A. I. Kruppa, V. S. Bashurova, T. V. Leshina and L. D. Kispert (2002) The role of radicals in the phototransformations of β-ionone in the presence of electron donors in solution. J. Photochem. Photobiol. A, Chem. 153, 113–119.
- Abarbri, M., J.-L. Parrain, A. Duchêne and J. Thibonnet (2006) Stereoselective synthesis of trienoic acids: Synthesis of retinoic acids and analogues. *Synthesis* 17, 2951–2970.
- Yang, M., Q.-R. Peng, J.-B. Lan, G.-F. Song and R.-G. Xie (2006) CaCl₂- or MgCl₂-catalyzed allylic oxidations of ionone-like dienes. *Synlett* 16, 2617–2620.
- Fráter, G., J. A. Bajgrowicz and P. Kraft (1998) Fragrance chemistry. *Tetrahedron* 54, 7633–7703.
- Huber, S. N. and M. P. Mischne (1995) A simple and efficient approach for the synthesis of a 1,2,4-trioxane related to the artemisinin. *Nat. Prod. Lett.* 7, 43–46.
- Mischne, M. P., S. N. Huber and J. Zinckzuk (1999) Photochemical reaction of β-ionone derivatives in the presence of oxygen. A convenient synthesis of substituted 1,2,4-trioxanes. *Can. J. Chem.* 77, 237–241.
- Borsarelli, C. D., S. G. Bertolotti and C. M. Previtali (2002) Thermodynamic changes in the photoinduced proton-transfer reaction of the triplet state of safranine-T. *Photochem. Photobiol. Sci.* 1, 574–580.
- Rios, A. O., A. Z. Mercadante and C. D. Borsarelli (2007) Triplet state energy of the carotenoid bixin determined by photoacoustic calorimetry. *Dyes Pigments*. 74, 561–565.
- Montenegro, M. A., I. L. Nunes, A. Z. Mercadante and C. D. Borsarelli (2007) Photoprotection of vitamins in skimmed milk by aqueous soluble lycopene—gum arabic microcapsule. J. Agric. Food Chem. 55, 323–329.
- Mousseron-Canet, M., J.-C. Mani and J.-P. Dalle (1967) Photooxydation sensilibiliseé dans la sérié de la β-ionone. Bull. Soc. Chim. 2, 608–612.
- Büchi, G. and N. C. Yang (1957) Light-catalyzed organic reactions. VI. The isomerization of some dienones. J. Am. Chem. Soc., 79, 2318–2323.
- van Wageningen, A., H. Cerfontain and J. A. J. Geenevasen (1975) Photochemistry of non-conjugated dienones. Part V. Photolysis of (E)-β-ionone and its isomeric α-pyran. J. Chem. Soc. Perkin II 12, 1283–1286.
- Cerfontain, H., J. A. J. Geenevasen and P. C. M. van Noort (1980) Photochemistry of dienones. Part 7. On the photosensitized isomerization of (E)-β-ionone and its isomeric α-pyran. Evidence for exciplex formation between the α-pyran and Fluoren-9-one. *J. Chem. Soc. Perkin II* 7, 1057–1062.
- 21. Marvell, E. N., G. Caple, T. A. Gosink and G. Zimmer (1966) Valence isomerization of a *cis*-dienone to an α -pyran. J. Am. Chem. Soc. **88**, 619–620.
- Wilkinson, F. and J.G. Brummer (1981) Rate constants for the decay and reactions of the lowest electronically excited state of molecular oxygen in solution. J. Phys. Chem. Ref. Data. 10, 809–999.
- Becker, R. S., R. V. Bensasson, J. Lafferty, T. G. Truscott and E. J. Land (1978) Triplet excited states of carbonyl-containing polyenes. J. Chem. Soc. Faraday Trans. 2. 74, 2246–2255.

- Chattopadhyay, S. K., C. V. Kumar and P. K. Das (1985) Triplet excitation transfer involving β-ionone. A kinetic study by laser flash photolysis. *Photochem. Photobiol.* 42, 17–24.
- Rudzki, J. E., J. L. Goodman and K.S. Peters (1985) Simultaneous determination of photoreaction dynamics and energetics using pulsed, time-resolved photoacoustic calorimetry. J. Am. Chem. Soc. 107, 7849–7854.
- Nonell, S., C. Martí, I. García-Moreno, A. Costela and R. Sastre (2001) Opto-acoustic study of tinuvin-P and rhodamine 6 G in solid polymeric matrices. *Appl. Phys. B* 72, 355–360.
- Feiss, A., B. Wegewijs, W. Gärtner and S. E. Braslasvky (1997) The role of triplet state in retinal photoisomerisation as studied by laser induced optoacoustic spectroscopy. J. Phys. Chem. 101, 7620–7627.
- 28. Martí, C., O. Jürgens, O. Cuenca, M. Casals and S. Nonell (1996) Aromatic ketones as standards for singlet molecular oxygen $O_2(^{1}\Delta_g)$ photosensitization. Time-resolved photoacoustic and near-IR emission studies. *J. Photochem. Photobiol. A, Chem.* **97**, 11–18.
- Lambert, C. and R. W. Redmond (1994) Triplet energy level of β-carotene. Chem. Phys. Lett. 228, 495–498.
- 30. Montenegro, M. A., M. A. Nazareno and C. D. Borsarelli (2007) Kinetic of the photosensitized oxygenation of the flavanone

naringin and its chalcone. J. Photochem. Photobiol. A, Chem. 186, 47-56.

- Montenegro, M. A., M. A. Nazareno, E. N. Durantini and C. D. Borsarelli (2002) Singlet oxygen quenching ability of carotenoids in a reverse micelle membrane mimetic system. *Photochem. Photobiol.* 75, 353–362.
- Stratton, S. P., W. H. Schaeffer and D. C. Liebler (1993) Isolation and identification of singlet oxygen oxidation products of β-carotene. *Chem. Res. Toxicol.* 6, 542–547.
- Baron, M. H., M. J. Coulange, C. Coupry, D. Baron, J. Favrot and M. M. Abo Aly (1989) *All-trans* retinal photoisomerization and photooxidation from UV laser radiation. Vibrational assignment of all-trans 5,8-peroxyretinal. *Photochem. Photobiol.* 49, 739–743.
- 34. Etoh, H., K. Ina and M. Iguchi (1973) Photosensitized oxygenation of α -pyran derived from β -ionone. *Agric. Biol. Chem.* **37**, 2241–2244.
- 35. Adam, W. and A. G. Griesbeck (1995) Photooxygenation of 1,3-dienes. In CRC Handbook of Organic Photochemistry and Photobiology, Chapter 25 (Edited by W. M. Horspool and P.-S. Song), pp. 311–324. CRC Press, Boca Raton, FL.
- Tietze, L. F. (1996) Domino reactions in organic synthesis. *Chem. Rev.* 96, 115–136.