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Journal of Photochemistry and Photobiology A: Chemistry 128 (1999) 65–74

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Single electron transfer in the phototransformations of β-ionone in the presence of electron acceptors

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Received 12 October 1998; received in revised form 22 June 1999; accepted 23 June 1999

Abstract

Single electron transfer (SET) in the photoreaction of (*E*)-β-ionone (**I**) and its derivatives with electron acceptors (quinones) has been detected in acetonitrile by CIDNP techniques. Analysis of CIDNP data has shown that the radical cation of **I** is formed during its photolysis in the presence of chloranil (CA), 2,5-dichlorobenzoquinone, and 2,3-dichloro-5,6-dicyanobenzoquinone. In the presence of benzo- and duroquinones (DQ), the radical cation is generated from the isomer of **I**, α-pyran (**II**). Consideration of combined CIDNP, EPR and electrochemical data, and quantum chemical analysis has demonstrated that the radical cations of **I** and **II** do not undergo *cis–trans* isomerization. It was suggested that in the reaction under study, adducts of **I** and **II** with quinones are possible precursors of the isomerized (*Z*)-β-ionone. Data favoring formation of two types of adducts, 2 + 2 cycloadditions of CA to **I**, and ethers resulting from **I** and **II** and quinones (CA, DQ), have been obtained. ©1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carotenoids and their radical cations have been a subject of numerous studies in the past decade, since such polyenes are components of many biological systems [1,2]. For example, processes of single electron transfer between carotenoids and acceptors are included in the photosynthetic schemes [3]. The main role of carotenoids as drugs appears to be the scavenging of toxic free radicals and preventing the formation of damaging singlet oxygen. However, there are only few examples of direct detection of the radicals of carotenoids [4–6].

On the other hand, geometrical *cis–trans* isomerization is a common transformation of carotenoids. The role of paramagnetic intermediates in the process of *cis–trans* isomerization of the substituted olefins by action of electron donors and acceptors is well known [7]. Recently, radical ions have been detected during the photolysis of all-*trans* retinal in the presence of electron donors and acceptors [8].

This paper presents the attempt to detect radical cations formed during photolysis of β-ionone and its derivatives in the presence of electron acceptors (quinones) in polar media by means of CIDNP. (*E*)-β-ionone was chosen as an object of the present investigation, since its photochemistry has been well studied [9–11]. Usually four isomers of β-ionone are discussed as phototransformation products. Scheme 1.

It was planned to elucidate the effect of electron acceptors on the phototransformations of **I**, including *cis–trans* isomerization. The structure of radical ions involved in photoprocesses would be established by comparison of CIDNP data with the results of quantum chemistry calculations of spin density distribution and with experimental EPR data, if applicable.

2. Experimental

2.1. Chemicals

(*E*)-β-ionone (Sigma) was used as supplied. The isomeric α-pyran (**II**) was obtained from **I** as described earlier [12] and purified twice by silica gel (260 mesh, Merck) column (length = 50 cm, *d* = 1 cm) chromatography, using hexane/Et_2O (15 : 1 v/v) as eluent. Benzoquinone (BQ), duroquinone (DQ), chloranil (CA), 2,5-dichlorobenzoquinone (DBQ) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) were purified by sublimation or recrystallization. Commercial deuterated solvents (Isotop, Russia) were used as supplied. Solutions of **I** (2–200 mM) and quinones (1–100 mM) in deuterated solvents were deaerated before irradiation by Ar bubbling for 10 min.

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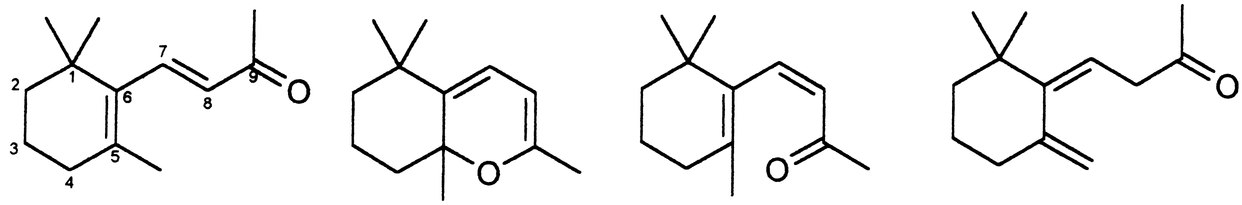
PII: S1010-6030(99)00140-9



(E)-β-Ionone **I** α-Pyran **II** (Z)-β-Ionone **III** (Z)-retro-γ-Ionone **IV**

Scheme 1.

Table 1
Absorption maxima and molar extinction coefficients of β-ionone isomers and quinones in acetonitrile

Compound	$\lambda_{max}(\varepsilon)$	ε(308 nm)	λ_{end}[a]
(*E*)-β-ionone (**I**)	291(12,000)	9000	370
(*Z*)-β-ionone (**II**)	285(4750)	2000	340 [11]
α-pyran (**III**)	285(1350)	900	340 [11]
BQ	285(1400)	230	500
DQ	278(2600)	132	490
CA	285(10,000)	400	420

[a] λ_{end}: the absorption band cut-off.

2.2. CIDNP experiments

Samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of the NMR spectrometers at room temperature. Steady state (SS) experiments were carried out using JNM FX-90Q (JEOL) NMR spectrometer (90 MHz ^{1}H operating frequency) with a home-made setup for photo-CIDNP observation. The light source was a high-pressure mercury lamp (1 kW) with thermal filter and light bandpass glass filter ($280 < \lambda_{trans} < 380$ nm). The light transmission band covers the absorption wavelengths of the quinones and isomers **I–III** (see Table 1).

Time-resolved (TR) [13] and quasi steady state (QSS) [14] CIDNP experiments were performed using an AM-250 (Bruker) NMR spectrometer (250 MHz ^{1}H operating frequency) with the photo-probehead (Bruker). An excimer laser EMG 101 MSC (Lambda Physik) was used as the light source (XeCl, $\lambda = 308$ nm, pulse duration 15 ns, energy per pulse 100 mJ). It is evident from Table 1 that at $\lambda = 308$ nm, $\varepsilon(\mathbf{I}, \mathbf{II}, \mathbf{III}) > \varepsilon(Q)$.

2.3. EPR and CV measurements

For EPR experiments and cyclic voltammetry (CV) anhydrous acetonitrile (Aldrich, 99.8%, residual water < 0.005%) was used as received. The tetrabutylammonium hexafluorophosphate (TBAHFP) (Fluka, polarographic grade) was used as supplied and stored in a dry box under nitrogen. Solutions of supporting electrolyte, 0.1 M TBAHFP, were prepared in a dry box. Electrolyte solution and the α-pyran were transferred by syringe to a septum-stoppered volumetric flask. Before the experiments, the solutions were deaerated by argon bubbling for 10 min. The concentration of **II** used for CV and EPR measurements was 5 mM. The CV of **II**, was recorded using a 1 mm disk Pt electrode and the BAS-100 W electrochemical an analyzer. EPR experiments were carried out with a commercial electrochemical flat cell using a Varian E-12 EPR spectrometer. EPR spectra were recorded under bulk electrolysis (BE) conditions using BAS-100 W. The potential for BE exceeded the potential of the first oxidation wave of **II** by 100 mV. The magnetic field was measured with a Bruker EPR 035M gaussmeter, and the microwave frequency was measured with a HP 5245L frequency counter.

2.4. Isomerization kinetics

Solutions of **I** and quinone (both 20 mM) were used to measure isomerization kinetics. The samples were irradiated in the probe of the JEOL NMR spectrometer for 15 min with the filter $\lambda_{trans} < 380$ nm at room temperature until photostationary conditions were attained. The spectra of products were recorded with an AM-250 NMR spectrometer immediately after irradiation and an hour later. The ratios of isomers were determined on the basis of the integral intensities of NMR signals of isomers.

2.5. HFI calculations

The calculations of hyperfine induced (hfi) constants of radical cations of isomers **I–III** were carried out by the PUHF/INDO (INDO approximation of Projected Unrestricted Hartree-Fock) method for geometrical conformations previously optimized by AM1 (MOPAC 5.0) [15].

3. Results

3.1. Reaction systems

The possibility of photoinduced electron transfer is defined by the Weller–Zachariasse criterion [16]:

Table 2
Excitation energies (eV) and polarographic half-wave potentials ($E_{1/2}$, V versus SCE) of the compounds under study

1Compound	$^{*}E^{\mathrm{S}}$	$^{*}E^{\mathrm{T}}$	$E_{1/2}{}^{+}$	$E_{1/2}{}^{-}$	ΔH(**I**)	ΔH(**II**)	Ref.
I	3.09	2.20[a]	1.89	−1.85			[9,11]
II		2.30[a]	1.29[b]	−1.75			[9,11]
BQ	2.59	2.18		−0.51	2.40	1.71	[27,28]
DQ		2.56		−0.76	2.65	1.96	[27,29]
DBQ				−0.18	2.07	1.38	[30]
CA		2.35		0.01	1.88	1.19	[27,30]
DDQ				0.50	1.49	0.70	[27]

[a] Highest estimated value [9,11].

[b] Data of the present study obtained from CV of **II**.

$$\Delta G_1 = \left(E^{+}_{1/2} - E^{-}_{1/2} - \frac{e^2}{\varepsilon_a R}\right) - {}^{*}E^{\mathrm{S,T}}$$

$$\Delta G_2 = {}^{*}E^{\mathrm{T}} - (E^{+}_{1/2} - E^{-}_{1/2} - e^2_a/\varepsilon_a R)$$

The excited state energies of the compounds ($^{*}E^{\mathrm{S}}$ and $^{*}E^{\mathrm{T}}$), their half-wave potentials and enthalpies of formation of possible radical ion pairs (RIP) in the reactions under study ($\Delta H = E_{1/2}{}^{+} - E_{1/2}{}^{-}$) are shown in Table 2. Energy of the Coulomb interaction of radical ions in RIP ($e^2_o/\varepsilon_{\mathrm{a}}R$, where R is the distance between radical ions in RIP, usually 0.7–1.0 nm) is equal to or less than 0.1 eV in acetonitrile.

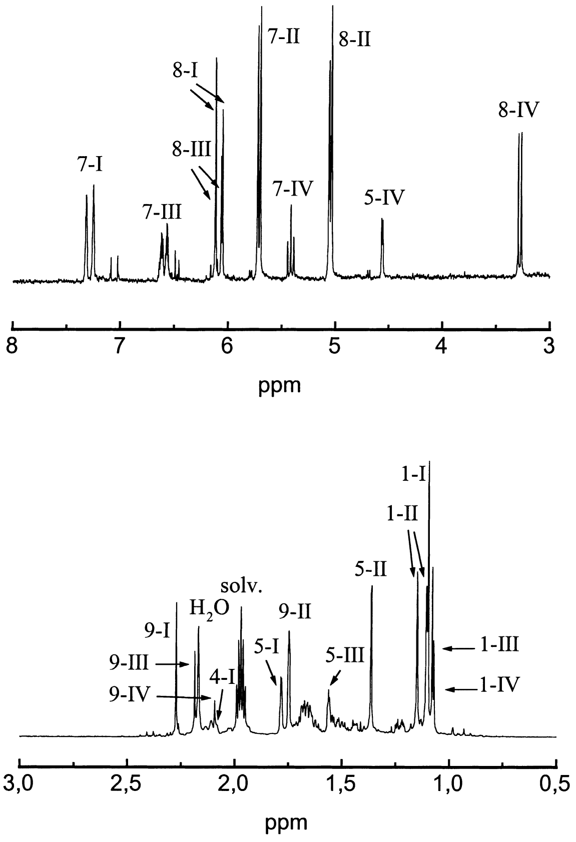


Fig. 1. ^{1}H NMR (250 MHz) spectrum of the isomers of β-ionone detected after irradiation of **I** in acetonitrile.

The condition $\Delta G_1 < 0$ determines the possibility of photoinduced electron transfer. Since the singlet excited state of quinone has a very short lifetime (10^{-11} s [17]), while the lifetime of the triplet state is about several microsecond [18], one might expect the quenching of triplet excited quinones by ionones. The triplet state of **I** (lifetime 180 ns [10]) could also react ($\Delta G_1 < 0$) with strong acceptors (CA, DDQ, DBQ). Since the lifetime of the singlet excited state of **I** is very short [12], it cannot be quenched to any appreciable extent by the amounts of quinones used in our experiments, even in the case of diffusion controlled quenching rate constants. $\Delta G_2 < 0$ points to the possibility of back electron transfer in the triplet radical ion pair leading to the formation of products in the excited triplet state.

As mentioned above, formation of the ^{3}RIP [$\mathbf{I}^{\bullet+}$ $\mathrm{Q}^{\bullet-}$] is possible in the reaction of **I** with CA, DBQ and DDQ. As follows from the data in Table 2, however, for weak acceptors (BQ and DQ), electron transfer is more probable in the case of **II**.

3.2. Photoisomerization

Figs. 1–3 show the ^{1}H NMR spectra recorded after UV irradiation of **I** in CD_3CN in the presence of CA (Fig. 2) or

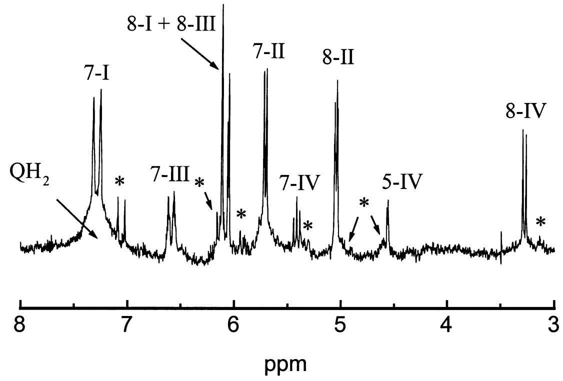


Fig. 2. ^{1}H NMR (250 MHz) spectrum observed after the photolysis of the mixture of **I** and CA, both 10 mM, in acetonitrile. Nonisomeric products are marked by an asterisk (*).

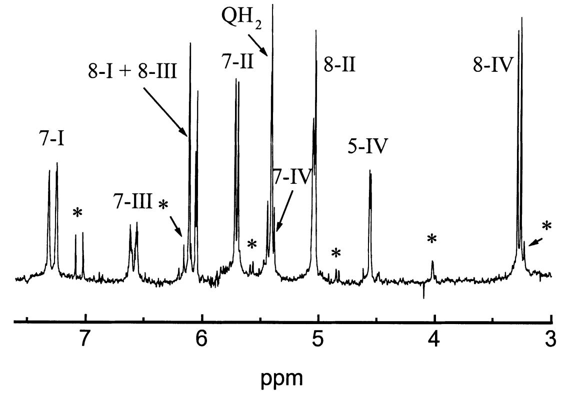


Fig. 3. ^{1}H NMR (250 MHz) spectrum of the products of the photolysis of **I** in the presence of DQ, both 10 mM, in acetonitrile. The nonisomeric products are marked by asterisk (*).

Table 3
^{1}H NMR chemical shifts of β-Ionone isomers in CD_3CN (ppm)[a]

Compound	1-CH_3	2-CH_2	3-CH_2	4-CH_2	5-CH_3	7-H	8-H	9-CH_3
I	1.09	1.52	1.65	2.10	1.78	7.28	6.08	2.27
II	1.10; 1.14				1.35	5.75	5.04	1.74
III	1.07			2.05	1.55	6.59	6.06	2.18
IV	1.06				4.56; 5.03[b]	5.41	3.28[c]	2.11

[a] Due to significant signal overlap some data are not shown.
[b] Non-equivalent=CH_2 protons.
[c] CH_2 – protons.

Table 4
Yields of isomers (% from initial β-ionone) after 15 min of irradiation of 20 mM solution of **I** in CD_3CN in the presence of quinones (20 mM). Same data after 1 h standing in the dark after irradiation (in parentheses)

Isomers	Direct irr.	CA	DQ
I	26(25)	11(11)	24(24)
II	40(50)	16(19)	22(41)
III	22(14)	11(7)	28(13)
IV	12(11)	6(6)	15(13)

DQ (Fig. 3) as well as in the absence of acceptors (Fig. 1). ^{1}H chemical shifts of isomers **I–IV** are given in Table 3. The kinetics of isomer formation for these cases was studied by means of NMR spectroscopy, and the results are shown in Fig. 4. The yields of isomers under photostationary conditions are presented in Table 4.

3.3. CIDNP

Since the chemical shifts of the isomers differ considerably, CIDNP effects for all isomers can be identified with high reliability. CIDNP effects of the β-ionone isomers were only observed in deuteroacetonitrile (Figs. 5 and 6 and Table 5). There are no CIDNP effects of isomers in C_6D_6 and CD_2Cl_2. Note that in the photolysis of **I** in CD_3CN and C_6D_6 in the presence of quinones the spectrum contains additional polarized lines (see Figs. 5 and 6).

3.4. EPR experiment

CV of a 5 mM solution of **II** shows a reversible wave with $E_{1/2}{}^{+} = 1.29$ V versus SCE (scan rate 100–1000 mV/sec). This value is close to the previously reported 1.20 V versus. SCE [9]. As noted above, in EPR experiments the potential for BE exceeded the first oxidation wave of **II** by about 100 mV. Under these conditions the EPR spectrum (Fig. 7) was resolved, showing a quintet with splitting about 0.51 mT and intensity distribution near to binomial. This spectrum is attributable to splitting by three methyl protons, and additional equivalent splitting by a single proton. The experimental value of the *g*-factor of the radical cation of **II** is 2.0037 ± 0.0001.

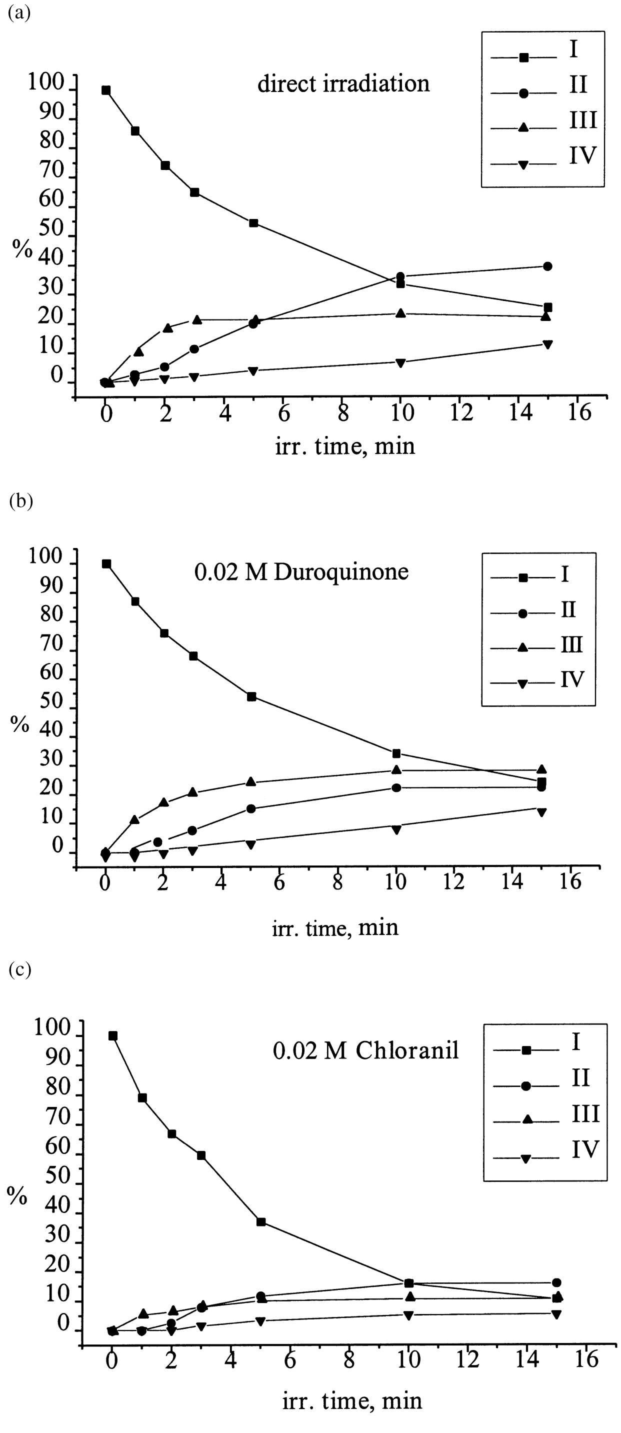


Fig. 4. Kinetics curves measured by means of NMR during the photolysis of **I**: (a) without acceptors (direct photolysis); (b) in the presence of DQ; (c) in the presence of CA.

4. Discussion

The major phototransformation pathways of **I** according to [9–11] in solution are presented in Scheme 2. Transformation of the triplet state of **I** leads to geometrical *trans–cis* isomerization around the C_7-C_8 double bond with the formation of **II** via **III**. (*Z*)-retro-γ-ionone (**IV**) is formed as a

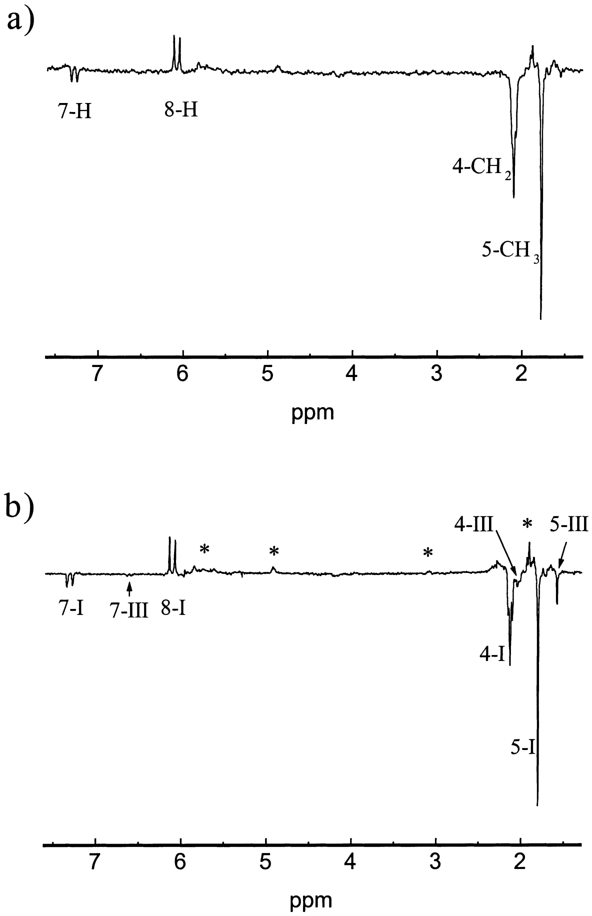


Fig. 5. CIDNP (250 MHz) spectra detected during the irradiation of **I** in the presence of CA, both 10 mM, in CD_3CN. (a) TR experiment, time delay 0.5 μs, PW = 2 μs, 32 scans; (b) QSS experiment, PW = 4 μs, 8 laser pulses per scan, 16 scans.

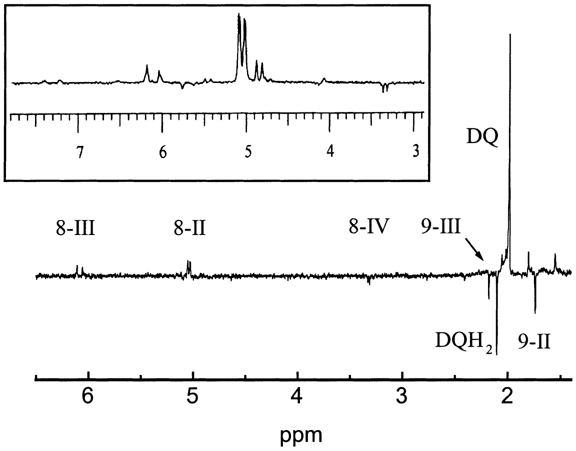


Fig. 6. QSS ^{1}H CIDNP (250 MHz) spectrum observed during irradiation of **I** (2 mM) in the presence of DQ (20 mM) in CD_3CN, PW = 4 μs, 8 laser pulses per scan, 32 scans. Inset: SS ^{1}H CIDNP (90 MHz) spectrum detected during the irradiation of **I** (50 mM) in the presence of DQ (100 mM) in CD_3CN.

primary photoproduct from excited singlet state of **I** [9]. It has been suggested that the isomeric α-pyran results from **III** in a dark reaction [9,10].

Fig. 4 represents the kinetic data on the direct isomerization of β-ionone and measured in the presence of quinones (see results). Analysis of the kinetic curves obtained for the photolysis of **I** in the presence and absence of quinones shows the remarkable influence of chloranil and duroquinone on the yields of isomers. In particular, comparison of the kinetic curves obtained for the direct photolysis (Fig. 4a) and the photolysis in the presence of duroquinone (Fig. 4c) leads to the following conclusions. Similarity of the kinetic curves obtained for the accumulation of **III** both in the presence and absence of quinone strongly suggests that in both cases, the formation of **III** occurs via direct photolysis of the initial *trans* isomer. Lower ratios of the yields **II/I** and **II/III** observed in the presence of duroquinone as compared to the case of direct photolysis show that duroquinone prevalently reacts with **II** leading to *cis*- and *trans*-ionones.

Photolysis of **I** in the presence of CA (Fig. 4b) shows only a minor extent of isomerization (the total yield of all isomers is far below 100%, see Table 4).This is the result of competition between direct isomerization of **I** and the reaction with CA. The absence of the additional intense lines in the olefinic region of the NMR spectra detected after prolonged photolysis of **I** and CA (Fig. 2) indicates that the final products do not possess proton-bearing double bonds. This could be the result of polymerization, since chloranil is known to be an effective initiator of polymerization of olefins [19]. In that case the polymers really have not C_7-C_8 double bonds.

We used CIDNP for the investigation of the elementary mechanisms of the interaction of β-ionone and its derivatives

Table 5
QSS ^{1}H CIDNP effects for various protons of the β-ionone isomers detected in the photolysis of **I**, **II** and mixture of isomers (see Experimental) in CD_3CN in the presence of quinones (A – absorption, E – emission)

	I	**II**	**III**	**IV**	**II**[a]	**I**[a]	**III**[a]
BQ	–	8(A)	–	8(E)			
DQ	–	8(A); 9(E)[b]	8(A); 9(E)[b]	8(E)	8(A), 9(E)[b]		9 (E)[b]
DBQ	4,5,7(E); 8(A)	–	–	–			
CA	4,5,7(E); 8(A)	–	–	–	8(A); 9(E)[b]	4,5,7(E); 8(A)	
DDQ	4,5,7 (E); 8(A)	–	–	–			

[a] CIDNP effects were detected during the photolysis of **II**.

[b] Positions 5 and 9 correspond to CH_3, and 4 to 4-CH_2 protons.

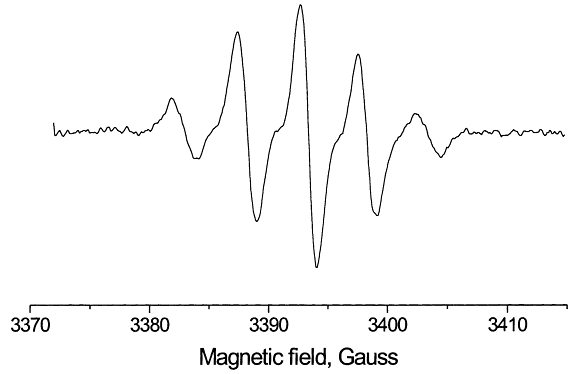
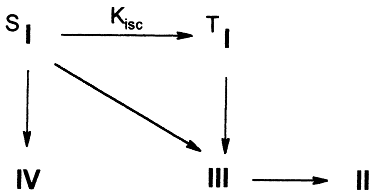


Fig. 7. EPR spectrum of the electrochemically generated radical cation of **II** in acetonitrile (supporting electrolyte 0.1 M TBAHFP).



Scheme 2.

Table 6
HFI constants (mT) calculated by the AM1/INDO method for radical cations of ionone isomers

	All-*trans*	*Cis–trans*	*Cis–trans*	*Cis*	α-pyran	α-pyran, exp.
φ_{6-7}	30°	174°	178°	−52.2°		
4-CH_2	2.80	2.35	2.92	1.75	−0.02	<0.05[a]
5-CH_3	1.76	1.38	1.70	1.40	0.01	<0.05
7-H	0.82	0.21	0.25	2.88	0.13	<0.1[a]
8-H	−0.30	−0.38	−0.26	−0.24	−0.29	0.51
9-CH_3	−0.33	−0.42	0.05	−0.22	0.46	0.51

[a] Estimated from linewidth of the EPR spectrum of the radical cation of **II**.

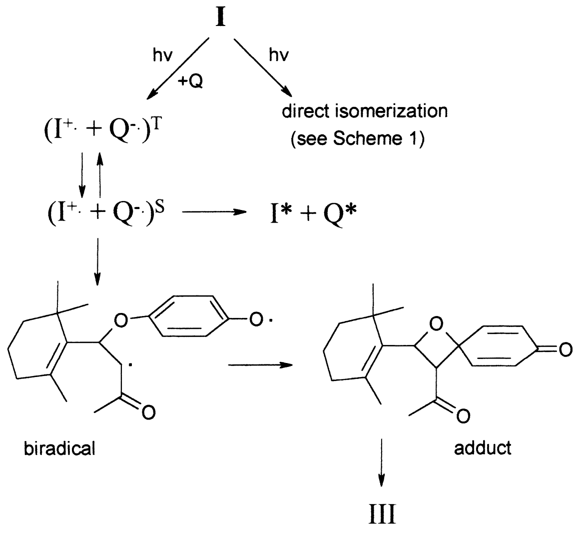
with acceptors of electrons. CIDNP effects were detected during the photolysis of **I** and **II** in the presence of all of the quinones (see Table 5 and Figs. 5 and 6).

Identification of the structure of polarized isomers of β-ionone was made by comparison of the signs and the ratio of intensities of polarized protons with the ratio of the calculated hfi constants of the radical cations of β-ionone and its isomers (see Table 6). The applicability of the calculated spin density distribution in unsaturated compounds was tested for the known radical-ions of stilbene and the experimentally determined parameters of the radical cation of **II**.

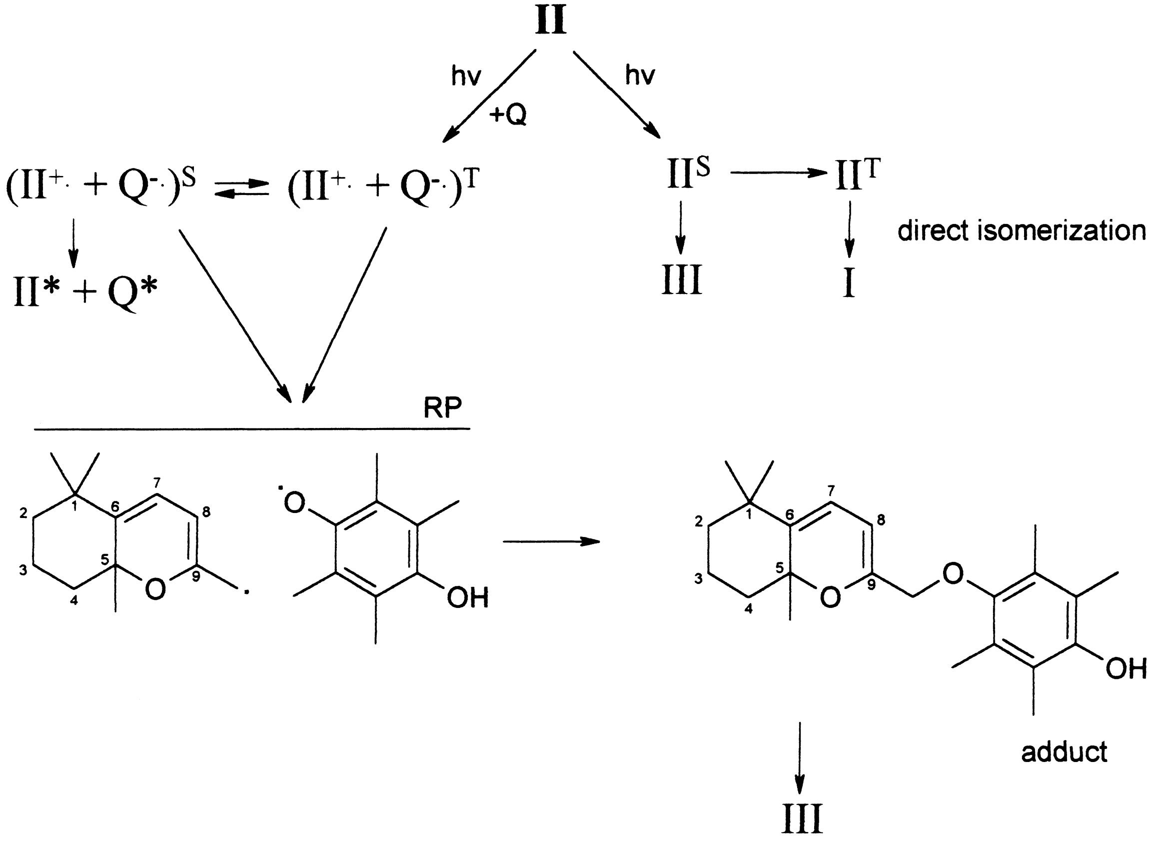
CIDNP effects of the protons of **I** had been observed during the photolysis of **I** in the presence of CA, DDQ and DBQ (Table 5 and Figs. 5 and 6). The appearance of CIDNP effects of β-ionone only in polar solvent (see results) leads to the conclusion that electron transfer is a primary act of the process [20]. In this case β-ionone could be polarized as a product of reverse electron transfer in the RIP of radical cation of **I** and radical anion of quinone.

The ratio of CIDNP intensities detected in TR experiments (Fig. 5a) for the 4-CH_2, 5-CH_3, 7-H and 8-H protons in **I** in the reaction with chloranil is $10:6:2.2:-3.2$, respectively. The ratio of calculated hfi constants of these protons for the *cis–trans* configuration of the radical cation is $10:5.9:0.9:-1.6$ (see Table 6) The absence of polarization of the 9-CH_3 protons is consistent with the small magnitude of calculated hfi constant of the *cis–trans* configuration of the radical cation of **I** with perpendicular orientation of the acyl group to the conjugated double bond ($\varphi_{8-9} = 90°$. see Table 6. Unfortunately, we have no additional arguments in favor of the configuration with $\varphi_{8-9} = 90°$. According to calculations [15] the rotation of this group at room temperature is free (energy barrier about 2 kcal/mol). The correspondence of the signs of experimental parameters to those of calculated hfi constants and qualitative agreement of CIDNP intensities with the spin density distribution in the radical cation of **I** allows one to conclude that CIDNP effects are present in the RIP of radical cation of **I** and radical anion of chloranil.

In QSS experiment during the photolysis of **I** in the presence of CA CIDNP effects were observed also for 4-H and 5-CH_3 protons of **III**. Positively polarized groups of broadened lines (5.50–5.90 ppm, and 4.95 ppm) were also detected (Fig. 5). Note that these signals are absent in the NMR spectra detected after the photolysis (Fig. 2). Probably these lines are due to a short-lived intermediate (adduct of **I** with CA).The origin of the polarization of **III** is not quite clear. According to the Kaptein rules [21], **I** is polarized as in-cage product of singlet RIP with a triplet precursor. According to modern theory [7] *cis–trans* isomerization can occur via the triplet excited state ($\Delta G_2 < 0$) or via the intermediacy of the radical ion. Since in the system under study $\Delta G_2 > 0$, the polarized *cis*-isomer (**III**) could result only by isomerization



Scheme 3.



Scheme 4.

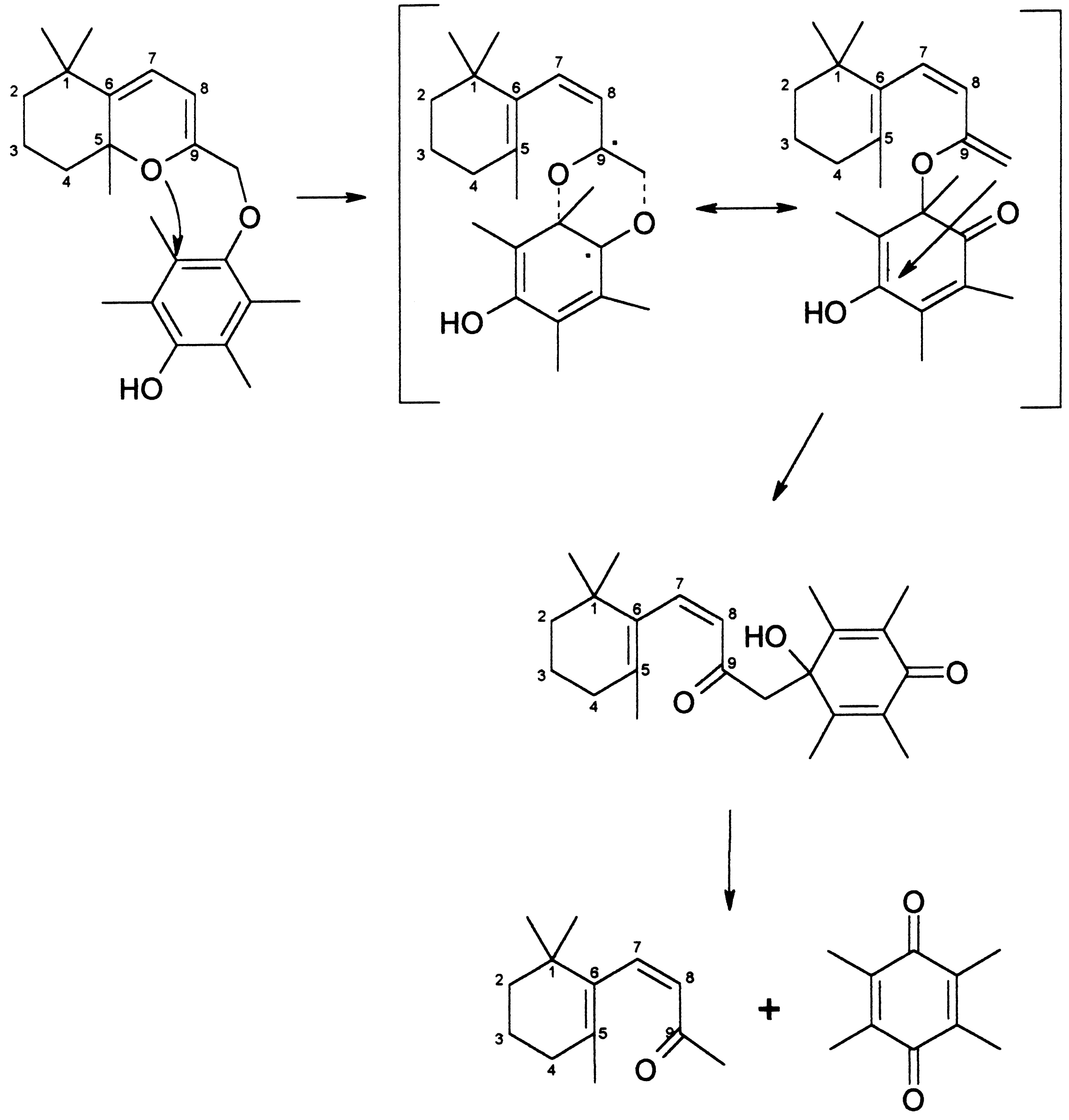
of the radical cation of **I**. In this case, polarization of **III** could be the in-cage type for very fast, or the *escape* type for slow, isomerization rate. However, TR experiments do not indicate polarization of **III**. This may indicate that isomerization of the radical cation of **I** is not responsible for the in-cage type polarization of **III** in the QSS experiments. Further, the results of quantum chemical calculations show that the energy barrier for twisting around the C_7-C_8 double bond in $\mathbf{I}^{\bullet+}$ is about 15 kcal [15]. This implies that, unlike in the long-chain carotenoids, this bond remains double in the radical cations of both *cis* and *trans* isomers. Consequently, one might suggest that the radical cation of **I** does not undergo isomerization to $\mathbf{III}^{\bullet+}$ within the time scale of the TR experiment.

On the other hand, the presence of polarized adducts of quinone and **I** for TR and QSS experiments suggests that **III** is a product of the adducts cleavage (Fig. 5). It has been shown earlier that [2 + 2] cycloadducts of olefins and quinones resulting from in-cage RIP recombination can decompose with the formation of geometric isomers of olefins [22,23] the present case formation of a cycloadduct involving C_7-C_8 of **I** and C–O bond of CA is preferable. A possible structure of the adduct is shown below: Scheme 3.

Thus, the appearance of CIDNP effect in the region 5.50–5.90 ppm might be due to 8-H proton of the adduct (Fig. 5). The observation of broad lines of polarized compounds and the absence of these lines in the spectra detected after the photolysis point to a short life-time of the adduct. As has been previously proposed formation and cleavage of such adducts involves a very short-lived biradical (23rd), with probability of geometric isomerization around the C_7–C_8 bond. In this case, CIDNP effects in the adduct were originated in the RIP of radical cation of **I** and radical anion of CA and then transfered to the protons of adduct and the *cis*-isomer (**III**). One might suggest that 7-H is close to the methyl group and could not be observed due to the overlap.

In the photoreaction of **I** with weak acceptors (DQ, BQ), where SET between quinones and the isomeric α-pyran is more likely than in the reaction of quinone with **I** (see Table 2), there is no polarization in TR experiments. In QSS experiments CIDNP effects of isomers (**II–IV**) were observed (Fig. 6). Note that the same pattern of CIDNP has been observed in the photolysis of **II** (see Table 5).

The appearance of chemical polarization of similar groups of protons of all three isomers (8H and 9-CH_3 of **I** and **III** and 8-CH_2 of **IV**, see Table 5) points to a unique paramagnetic precursor to all of the effects. Correspondence of CIDNP intensities of 8-H and 9-CH_3 with experimental values of hfi constants in the radical cation of **II** and with the signs of calculated hfi values at these positions (Table 6) is consistent with the hypothesis that the radical-cation of **II** is a common precursor of all polarized species.



Scheme 5.

Thus, polarization in isomers **II**–**IV** can be induced in RIP of $\mathbf{II}^{\bullet+}$ and quinone radical anion. Analysis of CIDNP signs [21] leads to the conclusion that **II** and **III** are polarized as in-cage recombination products of singlet RIP with a triplet precursor, and **IV** is an escape product of the same RIP. The analysis takes into account that *g*-factors of duroquinone radical anions (2.0044 [24]) are larger than those of the radical cations of **II** (2.0037, see results).

Thus, the α-pyran is polarized during the reverse electron transfer in the singlet state RIP. As mentioned above in that case the isomers could be formed only from the radical cation of **II**. However, EPR studies of the radical cation of **II** generated electrochemically showed its sufficient stability towards isomerization (see results). We, therefore, searched an alternate pathway responsible for the formation of isomers in the processes under study.

There are several unidentified lines in the NMR spectra observed during and after the photolysis of **I** in the presence of duroquinone (Fig. 6). There are three polarized lines: 4.85 (doublet A), 5.45 (doublet A), 4.10 (singlet A). The chemical shifts of these doublets are close to those of the 7-H and 8-H (5.04 and 5.75 ppm) of the α-pyran (see inset of Fig. 6). Polarized methyl protons of DQ (2.00, A) and DQH_2 (2.15, E) were also identified. Evidently, this additional product is the adduct of **II** and DQ.

Since the isomerization kinetics determined by NMR spectroscopy showed that the yield of the isomers in the reaction with DQ is about 100% (Fig. 4 and Table 4), that the adduct of **II** with DQ undergoes photocleavage followed by the formation of isomers.

The photoinitiated interaction between olefins and quinones described in the literature involves several processes [22,23,25]. In addition to the Paterno–Buchi cycloaddition reactions, addition of olefins to the O and C atoms of quinones might also take place [25]. However, since the chemical shifts of the additional polarized lines are similar to those of 7-H and 8-H in **II** (see Fig. 6), the most probable product is an ether-type adduct: Scheme 4.

One might expect that the first stage of the formation of the ether is also a single electron transfer. The next step would be the proton transfer resulting in the formation of the radical pair of hydroxyphenoxyl and neutral radical of **II**. The ether is the product of the recombination of this radical pair. It is assumed that proton is abstracted from the 9-CH_3 group, since, according to quantum-chemical calculations [15], maximum electron density in the radical cation of the α-pyran localizes on the oxygen atom, and this means that the 9-methyl protons should demonstrate significant acidity. Another argument in favor of this suggestion is the similarity (see Fig. 6) of the chemical shifts of 7-H and 8-H in the adduct to those in **II**; i.e., the C_7-C_8 double bond is present in the resulting adduct. The signal at 4.10 ppm can be assigned to the methylene group (9-CH_2) of the ether. The signals in the aliphatic region overlapped extensively and could not be analyzed.

According to the literature [26] O-allylarylethers can be subjected to Claisen photorearrangement resulting in *ortho* and *para* allylsubstituted phenols. CIDNP effects in Claisen rearrangement have been described for the ethers containing protons and methyl substituents in the aromatic ring [26].

The possible structure of the ether and the mechanism of the photorearrangement of arylpyranylethers are presented in the Scheme 5. The Claisen rearrangement involves migration of an allyl group in allylarylether to the para position of the aryl ring via the *ortho*-position. The migration occurs through cyclic transition states. It could be expected that the structure with the pyranyl fragment in the *para*-position would not be stable. Indeed, in the case of strong acceptors the corresponding ethers of **I** and **II** with these quinones have to be more stable than in the case of DQ, since the process of C-alkylation is not typical for CA (19th). Scheme 5.

5. Conclusions

The investigation of the photolysis of β-ionone in the presence of several quinones has demonstrated simultaneous direct isomerization of **I** and photoinitiated interaction of (*E*)-β-ionone and its isomeric β-pyran with quinones. This interaction in polar media starts with SET and competes with the direct photolysis of **I** and **II**. There are also data in favor of formation of isomerized **III** via cleavage of adducts of **I** with CA and **II** with DQ.

The appearance of CIDNP effect in nonpolar media in the region of 5–7 ppm (lines of the adducts) and simultaneous polarization of ionone derivatives in polar media, indicates two sources of CIDNP formation. Indeed, Scheme 5 includes both the RIP resulting from a single electron transfer between **I**, **II**, and quinones and the radical pair of free neutral radicals. In polar media, the contribution of RIP to observed CIDNP effect is prevalent. On the other hand, CIDNP induced in neutral radical pair is of much lower intensity and, therefore, in nonpolar media we observed only polarization of the adduct protons.

Acknowledgements

This work was supported by the US Civilian Research and Development Foundation (CRDF) under Grant RC1-175 and the Russian Foundation for Basic Research (RFBR) under Grant 98-03-32969. A.I. Kruppa thanks Young Investigator Research Opportunities of CRDF Collaborations Program of CRDF and RFBR for support. Laboratory supplies and EPR equipment were supported by the Division of Chemical Sciences, Office of Energy Research of the US Department of Energy under the Grant DE-F602-86ER13465.

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