

The influence of electron donors and acceptors on the isomer distribution in the photolysis of β -ionone

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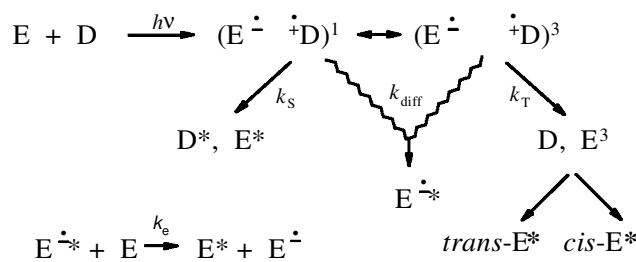
The application of the CIDNP technique has shown that geometrical *cis*–*trans* photoisomerization of β -ionone and its isomers in the presence of pyrene in polar media occurs via radical ion pairs. Based on the combined analysis of CIDNP results and kinetic data on the formation and decay of isomers, it has been demonstrated that this channel exerts a significant influence on the isomer distribution in this system and on the reaction with other electron donors and acceptors.

1. Introduction

In the last decade, the natural polyenes (carotenoids, retinoids, etc.) have attracted considerable attention due to their significant role in biology and medicine [1, 2]. In particular, it has been demonstrated that carotenoids not only participate in electron transport in photosystem II, and in the quenching of reactive oxygen species, but also they can serve as effective antioxidants. It is suggested that the majority of the reactions of naturally occurring polyenes proceed via donor–acceptor interaction followed the formation of radical ion pairs (RIPs). However, information on the reactivity of paramagnetic forms of polyenes is very scarce [3, 4].

The processes involving the paramagnetic forms of biologically important molecules (all-*trans*-retinal [5], horseradish peroxidase [6], coenzyme B₁₂ [7], amino acids [8, 9]) were investigated successfully by spin chemistry techniques (chemically induced dynamic nuclear polarization or CIDNP and the magnetic field effect or MFE). CIDNP techniques have been employed also to study the role of radical ions in the process of geometrical *cis*–*trans* isomerization, which is one of the most characteristic photoprocesses for polyenes [10–12]. The mechanism of isomerization involving an intermediate radical ion pair (so-called RIP-mediated isomerization) has been investigated for the case of phototransformation of substituted ethylenes in the presence of electron donors and acceptors [13, 14]. Spin chemistry methods were able to demonstrate that this mechanism prevails in polar media [13]. The key step of this mechanism is the formation of the excited triplet state of substituted ethy-

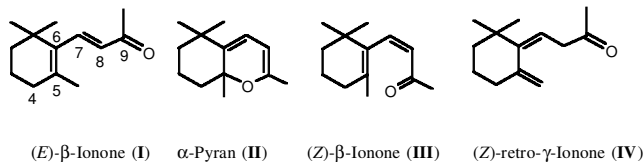
lene through back electron transfer in a triplet radical ion pair (see scheme 1).



Scheme 1.

Here E is *cis* or *trans* form of substituted ethylene, D is the electron donor, and * denotes the polarization. Similar mechanism has been proposed for the photolysis in the presence of electron acceptors.

The main difference between polyenes and substituted ethylenes is that the polyenes usually form a set of isomers. In particular, β -ionone, a short-chain natural polyene, has four main isomers (I–IV) detected in the direct and sensitized photolysis experiments [15–17].



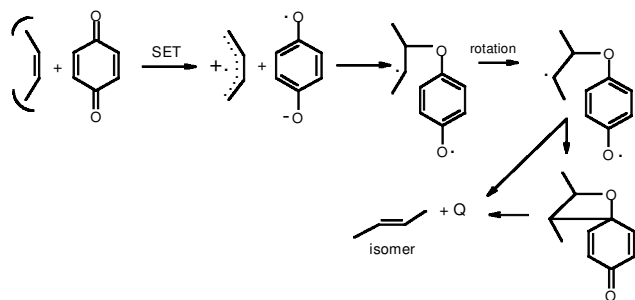
As a rule, the isomers have different triplet energies, redox properties, and hence different reactivities towards electron donors or acceptors.

Recently [10–12], the CIDNP technique has been used to demonstrate the participation of radical ions in

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photoisomerization or *trans*- and *cis*- β -ionone and also α -pyran. The photoisomerization has been investigated in the presence of electron acceptors (quinones), and donors (triphenylamine (TPA) and triphenylphosphine). It has been found that, in accordance with scheme 1, photoisomerization occurs only in the reaction with TPA where the RIP has enough energy for back electron transfer in the triplet state.

Geometrical *cis*-*trans* isomerization has been demonstrated to proceed also via short-lived intermediates: biradicals and diamagnetic adducts (with quinones [10]), and neutral radicals of β -ionone [11]. No isomerization of the radical anion or radical cation itself was observed by CIDNP [10–12]. The formation of diamagnetic adducts via an intermediate biradical is well known for photoreactions of quinones with molecules containing double bonds (Patterno–Buchi reaction [18, 19]). *cis*-*trans* isomerization is facilitated by the transformation of the double bond in the initial molecule to a single bond in the biradical.



Scheme 2.

This process was observed by CIDNP in the reaction of **I** with chloranil (formation of polarized *cis* isomer), and in the reaction of **II** with duroquinone (formation of polarized isomers **III** and **IV**).

A neutral radical of β -ionone could result from a radical anion through protonation in the presence of a hydrogen donor. Analysis of the calculated dependence of the heat of formation of the neutral radical shows that the twisting barrier around the C7C8 bond in the neutral radical is about 7 kcal mol⁻¹. At room temperature the estimated rate of *trans*-*cis* isomerization of the neutral radical is about 10⁶ s⁻¹. CIDNP results show that the *cis* isomer is the sole product of the isomerization of the *trans* form of the neutral radical.

The present paper reports the investigation of the RIP-mediated isomerization of β -ionone and its isomer α -pyran in the presence of pyrene by means of CIDNP. Of special interest are the situations where pyrene could play the double role of either the electron donor or electron acceptor, depending on the properties of the partner. This paper also attempts to analyse the contribution of the RIP-mediated isomerization to the present

process and those studied earlier [10, 11] on the basis of the combined analysis of CIDNP results and kinetic data on the accumulation and decay of isomers in the presence and in the absence of electron donors and acceptors.

2. Experimental

(*E*)- β -ionone (Sigma), triphenylamine (TPA) and pyrene (Py) (Aldrich) were used as supplied. Commercial deuterated solvent, CD₃CN, ('Isotop') was purified by distillation over P₂O₅. Solutions of **I** (2×10^{-3} – 2×10^{-1}) in CD₃CN in the presence of the electron donors (10^{-3} – 10^{-1} M) were deaerated by argon bubbling. The CIDNP techniques were described in detail in [10, 11] (see also [20]). Samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of the NMR spectrometer at room temperature. Time resolved and quasi steady state (QSS) CIDNP experiments were performed using a Bruker DPX-200 NMR spectrometer (200 MHz ¹H operating frequency), and a Lambda Physik EMG 101 MSC excimer laser was used as the light source ($\lambda = 308$ nm, 15 ns, 100 mJ). 0.02 M solutions of **I** and of the electron donors or acceptors in CD₃CN were used to measure the isomerization kinetics. The samples were irradiated using a high pressure mercury lamp (1 kW) with $\lambda < 380$ nm filter at room temperature until photostationary conditions were attained. The spectra of the products were recorded using the Bruker DPX-200 NMR spectrometer immediately after irradiation. The ratios of the isomers were determined from the integral intensities of their NMR signals.

3. Results

The time resolved CIDNP spectrum detected in the photolysis of **I** in the presence of pyrene demonstrates the only polarization effects attributed to initial β -ionone (4-CH₂ (A), 5-CH₃ (A), 7-H (E) and 9-CH₃ (A), figure 1(a)), where (A) denotes enhanced absorption and (E) denotes emission in the CIDNP spectrum. No time dependence was detected on the microsecond time-scale. This result could be regarded as evidence that β -ionone is polarized as the cage recombination product. The polarization pattern is in agreement with the hfi distribution in the β -ionone radical anion: $a_4 = 12$ G; $a_5 = 6.5$ G; $a_7 = -10$ G; and $a_9 = 6.5$ G [21].

The QSS CIDNP experiments demonstrate the significant dependence of the polarization pattern on the degree of isomerization. For low degrees of isomerization the CIDNP effects are similar to these obtained in time-resolved experiments. However, in the presence of even a small amount of isomers, the main polarized lines in the CIDNP spectrum were identified as the signals corresponding to the 8-H and 9-CH₃ groups of **I** and

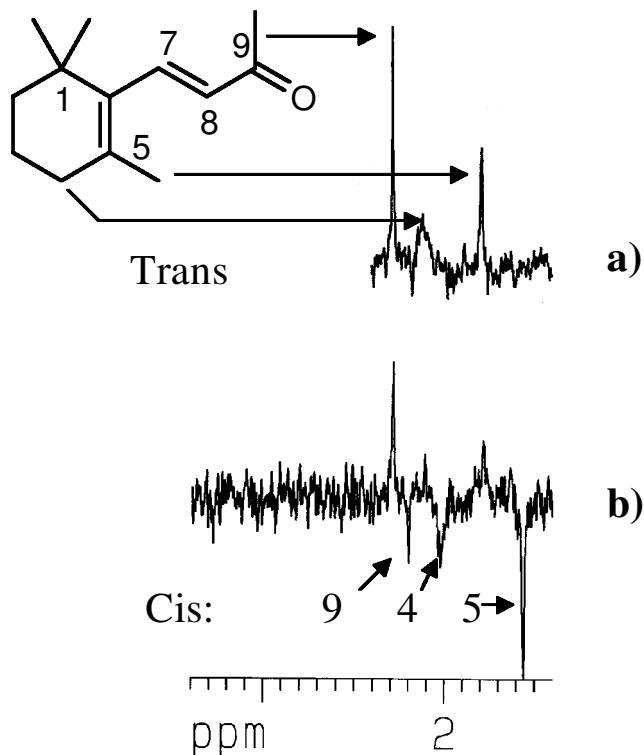


Figure 1. (a) Time-resolved ^1H CIDNP (200 MHz) spectrum detected during the irradiation of **I** in the presence of pyrene, both 10 mM, in CD_3CN . Time delay $0.5\ \mu\text{s}$, $\text{PW}=2\ \mu\text{s}$, 512 scans. (b) QSS experiment in the presence of acetic acid, $\text{PW}=6\ \mu\text{s}$, 64 scans, 8 laser pulses per scan.

II (figure 2). The photolysis of the same system in the presence of acetic acid leads to the appearance of polarized lines of *cis* isomers (4- CH_2 , 5- CH_3 and 9- CH_3) in the CIDNP spectrum (figure 1 (b)).

The kinetic traces of the decay and accumulation of isomers measured during the photolysis of β -ionone in

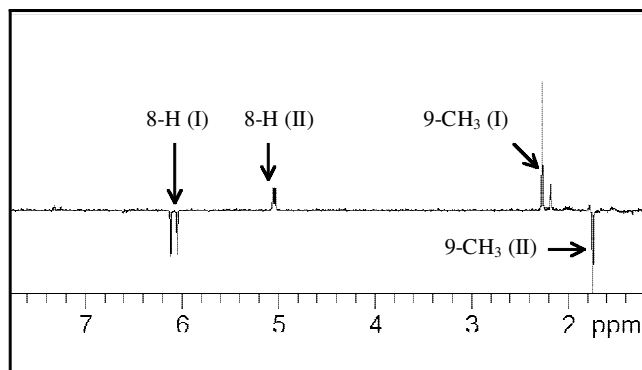


Figure 2. QSS ^1H CIDNP (200 MHz) spectrum observed during irradiation of the mixture of isomers **I–IV** in the presence of pyrene (10 mM) in CD_3CN , $\text{PW}=6\ \mu\text{s}$, 64 scans, 8 laser pulses per scan.

the presence of triphenylamine and pyrene are presented in figure 3. The corresponding kinetic curves for direct photolysis are shown for comparison. Table 1 lists the ratios of isomer concentrations under the photo-stationary condition.

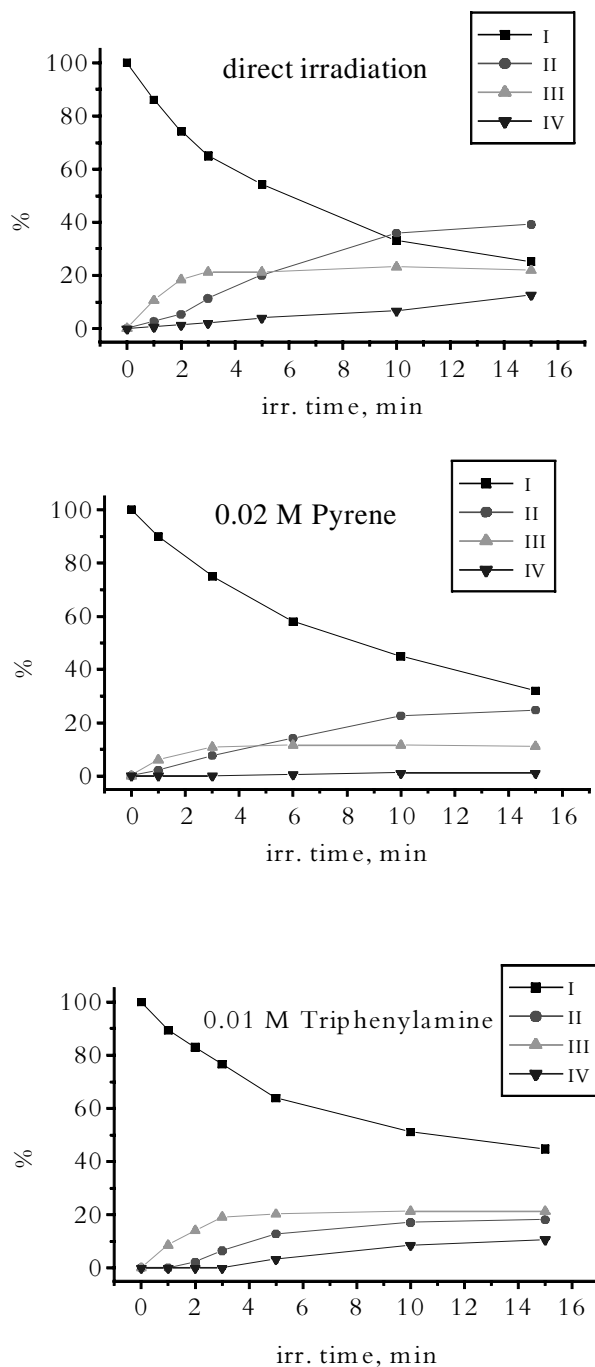


Figure 3. Kinetics of the decay and accumulation of isomers measured by ^1H NMR during the direct photolysis of **I** and during photolysis in the presence of pyrene and TPA (concentration of **I**, 20 mM).

Table 1. The ratio of isomers **I**–**IV** after 15 min irradiation in the absence and presence of electron donors and acceptors (see also figure 1 and [10] for chloranil and duroquinone)

	II/I	III/I	IV/I
Direct	1.55	0.9	0.5
TPA	0.4	0.48	0.24
Py	0.88	0.22	0.05
Duroquinone	0.9	1.1	0.5
Chloranil	1.5	1	0.5

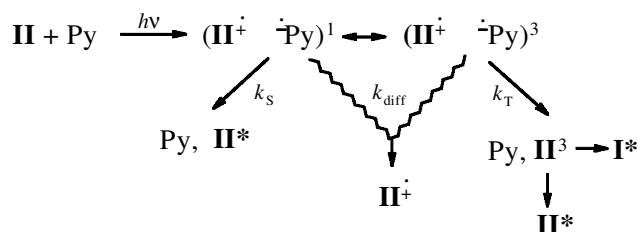
4. Discussion

An analysis of the time resolved CIDNP effects detected during the photolysis of **I** in the presence of pyrene using Kaptein rules [22] leads to the conclusion that **I** is polarized as a cage product of triplet RIP comprised of the radical anion of **I** and radical cation of pyrene. Because it is known [11] that back electron transfer in the triplet state of the RIP can result in the formation of triplet excited state of **I**, which is known to be the precursor of the *cis* isomer (**III**) [11, 16], one should expect the appearance of polarized lines of both **I** and **III** in the CIDNP spectrum. The absence of polarization of the *cis* isomer (**III**) and its low yield (see figures 1(a), 3 and table 1) could be explained by assuming that pyrene quenches the triplet state of **I**. The quenching of the triplet state of **I** can proceed due to the close values of triplet energies of β -ionone and pyrene ($E_T(\mathbf{I}) = 2.39$ eV and $E_T(\text{Py}) = 2.06$ eV [15, 16]). Another possible reason for the absence of the polarized *cis* isomer could be the formation of triplet excited states of Py (but not β -ionone) via back electron transfer in this RIP.

After the accumulation of even a small amount of isomers in the reaction mixture the CIDNP pattern changed (cf. figures 1 and 2). NMR signals corresponding to the 8-H and 9-CH₃ groups of **I** and **II** become the main polarized lines in the CIDNP spectrum. The analysis of hfi constants and their distribution

in the suggested structures of all the possible paramagnetic particles participating in the reaction leads to the conclusion that such a CIDNP pattern could be explained if the effects are formed in the α -pyran radical cation ($a(8\text{-H}) = -5.2$ G and $a(9\text{-CH}_3) = 5.2$ G [10]). The application of Weller–Zachariasse criterion [23] shows that the formation of this RIP, (**II**⁺ Py^{•−}), is possible (see table 2). Thus, for β -ionone, pyrene plays the role of electron donor, while in the case of α -pyran it reacts as an electron acceptor.

An analysis of the polarization signs in the QSS experiments using Kaptein rules shows that **II** is the product of back electron transfer in the singlet state of this RIP, and **I** is the product of back electron transfer in the triplet state of the same RIP. Since the back electron transfer in the triplet RIP results in the formation of ³**II**, the CIDNP results allow one to conclude that **I** is the product of the transformation of ³**II**. Taking into account that the structure of **II** is closer to **III** than to **I**, this result might well seem to be unusual. Nevertheless, one might note the clear agreement with reference data [15, 16]. The photolysis of α -pyran in the presence of pyrene demonstrates the same CIDNP effects as shown in figure 2, confirming the suggested mechanism presented in scheme 3.



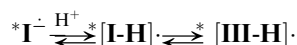
The appearance of polarized lines of the *cis* isomer (4-CH₂, 5-CH₃ and 9-CH₃) in the CIDNP spectrum during photolysis in the presence of acid points to the existence of the additional channel of *cis*–*trans* isomerization

Table 2. Excitation energies and polarographic half-wave potentials of the compounds under study (in eV). $\Delta H = {}^{1/2} E_{\text{ox}}(\text{donor}) - {}^{1/2} E_{\text{red}}(\text{acceptor})$.

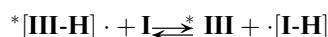
	$\epsilon(308 \text{ nm})$	E^S	E^T	${}^{1/2} E_{\text{ox}}$	${}^{1/2} E_{\text{red}}$	$\Delta H(\mathbf{I})^a$	$\Delta H(\mathbf{II})^a$	Ref.
I	9 000	3.09	2.39	1.89	−1.85			[15–17]
II	2 000		2.35	1.20				[15–17]
III	900							[16]
Duroquinone	130		2.56		−0.76	2.65	1.96	[24, 25]
Chloranil	400		2.35		0.01	1.88	1.19	[24, 25]
Py	20 000	3.38	2.08	1.06	−2.19	2.91	3.39 (II ⁺)	[17, 24]
TPA	30 000	3.61	3.05	0.92		2.77		[24, 25]

^a $\Delta H(\mathbf{I})$ and $\Delta H(\mathbf{II})$ correspond to RIPs with isomers **I** and **II**. In all cases $\Delta H > E^T(\mathbf{I}, \mathbf{II})$. It means that, according to the Weller–Zachariase criterion [23], the recombination of the RIP can proceed from both the singlet state with the formation of polarized products in ground state and from the triplet state with the formation of the corresponding isomers in the triplet excited state.

(figure 1 (b)). It is known [26], that the radical anion of **I** in the presence of hydrogen donors could be protonated, with the formation of the neutral radical:



The CIDNP pattern indicates that the polarization products of **I** and **III** are formed in the RIP comprised of the radical anion of **I** and radical cation of Py. The opposite signs of the polarization of the *cis* and *trans* isomers could be explained by the formation of the *cis* isomer in solution. It is known [20] that 'cage' and 'escape' products of the RIP demonstrate the opposite polarization signs and, since the *trans* isomer is polarized as the cage recombination product, it is assumed that the *cis* isomer is the escape product of the same RIP. The polarization may be transferred to a diamagnetic molecule via proton exchange:



This result confirms the earlier conclusion [11] about the possibility of the isomerization of the neutral radical of *trans*- β -ionone to the *cis* isomer in the photolysis of **I** in the presence of TPA.

It should be recalled that although the CIDNP technique provides unique information on the elementary mechanism of radical reactions, one could not estimate the contribution of the radical ion mechanism on the basis of an analysis of CIDNP data. For this purpose, the kinetic traces of the decay and accumulation of the isomers observed during the photolysis of **I** in the presence of electron donors and acceptors were compared with those for direct photolysis. Thus, the process of the direct isomerization of β -ionone will be used as a reference. As demonstrated earlier [10, 11] and re-stated below, direct isomerization is present in all experiments.

It had been reported by various investigators that direct photoisomerization of **I** proceeds from both singlet and triplet excited states [16, 27]. An analysis of kinetic traces of isomer formation during direct or sensitized photolysis has shown that *cis* isomer (**III**) of β -ionone results from triplet state of **I**, and α -pyran (**II**) results from ground state and excited singlet states of **III**. The participation of the excited triplet state of the *cis* isomer in the formation of **II** was also suggested from the data on sensitized photolysis [16]. The fourth main product, (*Z*)-retro- γ -ionone (**IV**), is suggested to form via the singlet excited states of all isomers **I-III**.

An analysis of the data from table 1 points to two different situations. In the photolysis in the presence of chloranil the isomer distribution is nearly identical to that observed for direct photolysis. For other reaction mixtures the distinction is significant, especially in the case of isomers **II** and **III**. Thus, a remarkable contribu-

tion from RIP-mediated isomerization is observed only in the situation when the RIP has enough energy for the formation of β -ionone or α -pyran in an excited triplet state (reaction with TPA and Py; see, for example, scheme 3). These results are in good agreement with the CIDNP data.

As shown earlier [10], in the case of chloranil, only reversible electron transfer takes place, and therefore isomers are formed mainly through direct photolysis. The special case of the photolysis with duroquinone has been described [10]. Duroquinone reacts only with one isomer, α -pyran, and this results in a decrease in the yield of this isomer (see table 1).

Now, let us try to analyse the kinetic curves detected in the present NMR study and compare them with the data for direct photolysis. As one can see, all the kinetic traces in the case of α -pyran always have an induction period. This observation is in accordance with the reference data on the formation of **II** from *cis* isomer **III** only, both under UV irradiation and in the dark.

As follows from the similar values of the optical densities of the reagents (see table 2), the light is adsorbed by isomers **I-III** as well as by their partners, TPA and Py. However, according to the data of table 2, the excited triplet states of **I-III** have insufficient energy for electron transfer with Py or TPA (Weller-Zachariasen criterion [23]). Thus, electron transfer occurs only in the case of the formation of excited states of the partners TPA or Py. Therefore, the contribution of direct isomerization is proportional to the ratio of the optical densities of the partners.

In the presence of pyrene, a significant decrease in the yield of **III** and especially **IV** was observed. The considerable decrease in the yield of the *cis* isomer confirms the suggestion that the reason for the absence of polarized *cis* isomer in the CIDNP experiment is the quenching of the triplet state of the precursor of **III** by pyrene. The decrease in the yield of **IV** is due to the decreased contribution from direct photolysis.

The different changes in the ratios **II/I** (fourfold decrease) and **III/I** (twofold decrease, see table 1) detected in the presence of TPA, is due to the formation of only isomers **I** and **III** via radical ion pairs. Since **II** is not formed via a RIP-mediated mechanism, its yield decreases significantly. The corresponding decrease in the rate of formation of **II** was also detected (see figure 3). Only a small decrease in the formation rate of **III** was detected in this system. This fact is in accordance with the CIDNP data, and means that the *cis* isomer is formed mainly via the intermediate radical ion pair.

Thus, these results point to the significant role of the presence of electron donors and acceptors in the process of *cis-trans* isomerization. The RIP-mediated mechanism

exerts a significant influence on the ratio and accumulation rate of isomers. The following conclusions have been drawn from an analysis of the CIDNP results and the time courses of the isomer formation. Only the *cis* isomer is formed via the RIP-mediated mechanism of isomerization of **I**, and only *trans*- β -ionone is formed via the RIP-mediated mechanism of isomerization of **II**. CIDNP results also confirm the reference data on the mutual transformation of isomers **I–IV**. It was demonstrated that **III** is formed from excited triplet state of **I**, and **I** is formed from the excited triplet state of **II**. Isomer **IV** results from the excited singlet states of all isomers **I–III**.

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References

- [1] TRUSCOTT, T. G., 1990, *J. Photochem. Photobiol. B*, **6**, 359.
- [2] EDGE, R., MCGARVEY, D. J., and TRUSCOTT, T. G., 1997, *J. Photochem. Photobiol. B*, **41**, 189.
- [3] KONOVALOVA, T. A., KONOVALOV, V. V., and KISPERS, L. D., 1997, *J. phys. Chem. B*, **101**, 7858.
- [4] TINKLER, J. H., TAVENDER, S. M., PARKER, A. W., MCGARVEY, D. J., MULROY, L., and TRUSCOTT, T. G., 1996, *J. Amer. chem. Soc.*, **118**, 1756.
- [5] POLYAKOV, N. E., BASHUROVA, V. S., SCHASTNEV, P. V., and LESHINA, T. V., 1997, *J. Photochem. Photobiol. A*, **107**, 55.
- [6] KRUPPA, A. I., TARABAN, M. B., LESHINA, T. V., NATARAJAN, E., and GRISSOM, C. B., 1997, *Inorg. Chem.*, **36**, 758.
- [7] TARABAN, M. B., LESHINA, T. V., ANDERSON, M. A., and GRISSOM, C. B., 1997, *J. Amer. chem. Soc.*, **119**, 5768.
- [8] HORE, P. J., WINDER, S. L., ROBERTS, C. H., and DOBSON, C. M., 1997, *J. Amer. chem. Soc.*, **119**, 5049.
- [9] TSENTALOVICH, YU. P., and MOROZOVA, O. B., 2000, *J. Photochem. Photobiol. A*, **131**, 33.
- [10] POLYAKOV, N. E., BASHUROVA, V. S., MUSIN, R. N., LESHINA, T. V., HAND, E. S., and KISPERS, L. D., 1999, *J. Photochem. Photobiol. A*, **128**, 65.
- [11] POLYAKOV, N. E., KRUPPA, A. I., BASHUROVA, V. S., LESHINA, T. V., and KISPERS, L. D., 2000, *J. Photochem. Photobiol. A*, in press.
- [12] POLYAKOV, N. E., LESHINA, T. V., and KISPERS, L. D., 2001, *RIKEN Rev.*, in press.
- [13] LESHINA, T. V., SALIKHOV, K. M., SAGDEEV, R. Z., BELYAEVA, S. G., MARYASOVA, V. I., PURTOV, P. A., and MOLIN, YU. N., 1980, *Chem. Phys. Lett.*, **70**, 228.
- [14] ROTH, H. D., and SCHILLING, M. L. M., 1980, *J. Amer. chem. Soc.*, **102**, 4303.
- [15] CERFONTAIN, H., GEENEVASEN, J. A. J., and VAN NOORT, P. C. M., 1980, *J. chem. Soc. Perkin II*, 1057.
- [16] CERFONTAIN, H., and GEENEVASEN, J. A. J., 1981, *Tetrahedron*, **37**, 1571.
- [17] CHATTOPADHYAY, S. K., KUMAR, C. V., and DAS, P. K., 1985, *Photochem. Photobiol.*, **42**, 17.
- [18] ECKERT, G., and GOEZ, M., 1994, *J. Amer. chem. Soc.*, **116**, 11999.
- [19] GOEZ, M., and ECKERT, G., 1996, *J. Amer. chem. Soc.*, **118**, 140154.
- [20] SALIKHOV, K. M., MOLIN, YU. N., SAGDEEV, R. Z., and BUCHACHENKO, A. L., 1984, *Spin Polarization and Magnetic Effects in Radical Reaction* (Budapest: Akademiai Kiado).
- [21] KRUPPA, A. I., KONOVALOV, V. V., LESHINA, T. V., and KISPERS, L. D., 1999, *J. chem. Phys.*, **103**, 1414.
- [22] KAPTEIN, R., 1971, *Chem. Commun.*, 732.
- [23] WELLER, A., and ZACHARIASE, K., 1967, *J. phys. Chem.*, **46**, 4984.
- [24] MANN, C. K., and BARNES, K. K., 1970, *Electrochemical Reactions in Nonaqueous Systems* (New York: Marcel Dekker).
- [25] BECKER, G. O., 1976, *Einführung in die Photochemie* (Berlin: VEB).
- [26] BOBROWSKI, K., and DAS, P. K., 1987, *J. phys. Chem.*, **91**, 1210.
- [27] VAN WAGNINGEN, A., CERFONTAIN, H., and GEENEVASEN, J. A. J., 1975, *J. chem. Soc. Perkin II*, 1283.

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