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Photoinduced transformation of matrix-isolated methyl 2-pyrone-3-carboxylate into methyl 2-pyrone-5-carboxylate via intramolecular hydrogen shift in open-ring aldehyde–ketene

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Abstract

Photochemical transformations of methyl 2-pyrone-3-carboxylate (**mp3c**) were studied by matrix-isolation technique. The dominating primary photoreaction induced by UV ($\lambda > 295$ nm) light was α -bond cleavage leading to open-ring aldehyde–ketene. Another reaction characteristic of α -pyrones, isomerisation to the Dewar form, did not occur for **mp3c**. The ring-opening photoreaction was followed by intramolecular hydrogen shift and subsequent ring-closure reaction converting the aldehyde–ketene into methyl 2-pyrone-5-carboxylate (**mp5c**). Upon prolonged UV irradiation, **mp3c** completely transformed into **mp5c** and its Dewar isomer **Dmp5c**. Unequivocal identification of **mp5c** and **Dmp5c** photoproducts was enabled by exact knowledge of their experimental IR spectra, recorded in separate experiments.

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1. Introduction

α -Pyrones are known to exhibit a rich photochemistry, which was studied for the compounds in solutions [1] and, more extensively, using the matrix-isolation technique [2–9]. It was found that irradiation of α -pyrones with UV light may induce either the ring-opening reaction, resulting in formation of the isomeric conjugated aldehyde–ketene, or ring-contraction to the Dewar structure (Scheme 1).

When the starting compound bears a hydrogen atom at the position 6, the open-ring photoproduct may undergo an intramolecular [1,5] sigmatropic hydrogen shift reaction, with the ketene and aldehyde groups converting into each other (Scheme 2).

In the case of unsubstituted α -pyrone, the reactant and product of the hydrogen shift reaction are the same due

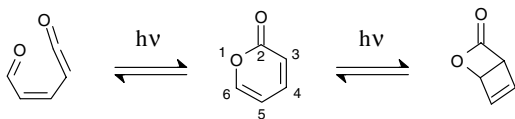
to the intrinsic symmetry of the system. However, introduction of a substituent in the pyran ring, at any position other than 4, lifts the symmetry relationship between the species before and after the hydrogen shift. This possibility has been used as a powerful experimental strategy in investigations on the chemistry of α -pyrones. In such a way, experiments with isotopic labeling (¹³C, ¹⁸O) showed migration of the isotopic label within the pyran ring (Scheme 3a and b) [9,10], whereas experiments with 3- and 5- methyl or deuterium substituted α -pyrones resulted in interchange of the positions (3 and 5) of these substituents (Scheme 3b and c) [10,11].

The common structural feature of all species depicted in Scheme 3 is the presence of a hydrogen atom at position 6. When this position is blocked by a methyl group, the migration of the isotopic label or of a substituent does not occur [10,12,13].

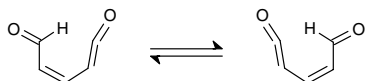
All the above mentioned observations can be explained in terms of the mechanism depicted in Scheme 4. According to this mechanism, the first step of the photoinduced ring-opening reaction yields the conjugated aldehyde–ketene. In

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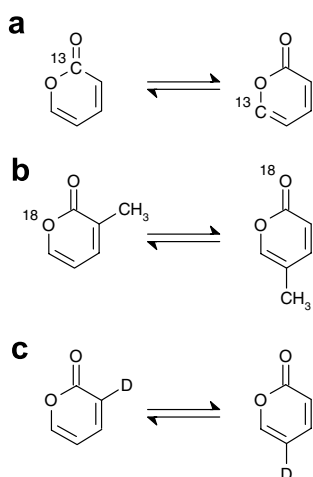
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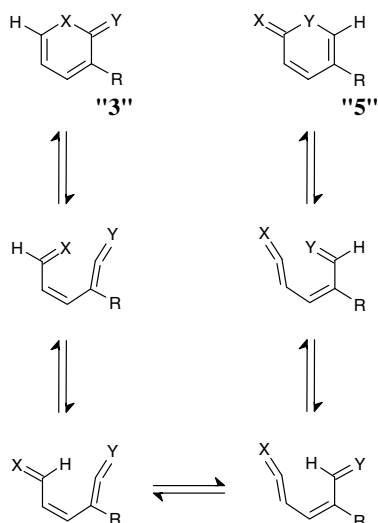
Scheme 1. UV-induced photochemical transformations of α -pyrone. The explicit numbering of the α -pyrone ring is included.



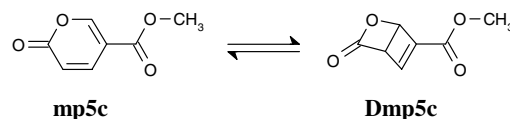
Scheme 2. Intramolecular hydrogen shift reaction in the open-ring aldehyde–ketene isomer of α -pyrone. The migrating hydrogen is shown explicitly.



Scheme 3. Experimentally observed [9–11] transformations in isotopically labeled α -pyrone and in α -pyrone derivatives.



Scheme 4. Mechanism of the ring-opening, [1,5] sigmatropic hydrogen shift and ring-closure reactions in the pyran (or thiopyran) ring. The migrating hydrogen (at position 6) is shown explicitly. X and Y represent heteroatoms (such as O or S). '3' and '5' indicate the position of substituent R.



Scheme 5. Experimentally observed [14] UV-induced transformation in matrix-isolated methyl 2-pyrone-5-carboxylate.

the second step, this species undergoes conformational isomerisation, so that the aldehyde hydrogen (explicitly shown in Scheme 4) adopts its position in the nearest vicinity of the ketene moiety and becomes well aligned for the [1,5] intramolecular migration. In the third step, the hydrogen shift occurs. The next two steps are similar to the first two elementary acts of the reaction, but occur in the opposite direction.

In pursuit of further representative examples, we have recently studied the photochemical behaviour of methyl 2-pyrone-5-carboxylate (**mp5c**) [14] (see Scheme 5). Monomers of this compound were deposited in an argon matrix at 10 K and subjected to UV irradiation [14]. The progress of the photoreactions induced by UV ($\lambda > 295$ nm) light is illustrated in Fig. 1.

The initial isomer of **mp5c** (with a planar, six-membered pyran ring) was transformed mainly into the Dewar photo-product **Dmp5c**, in which the position of the methyl-carboxylate substituent (with respect to the oxygen atom of

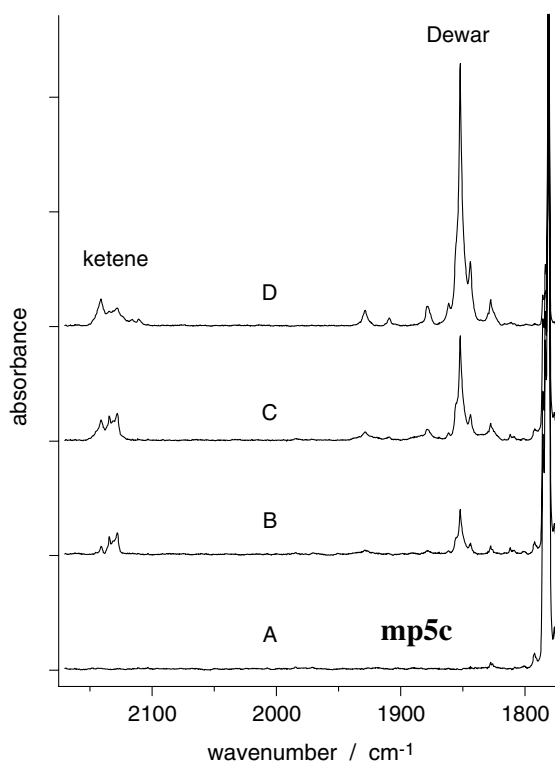


Fig. 1. Progress of photochemical changes induced by UV ($\lambda > 295$ nm) irradiation of methyl 2-pyrone-5-carboxylate (**mp5c**) isolated in an Ar matrix at 10 K. The spectra were recorded: (A) before irradiation, (B) after 5 min, (C) after 15 min and (D) after 100 min of irradiation.

the ring and to the carbonyl group) was conserved intact (Scheme 5).

The most characteristic IR spectral feature of the **Dmp5c** form is the band at 1852 cm^{-1} (Fig. 1). This band appeared in the IR spectrum already after a very short period of irradiation. On the other hand, a multiplet band at $2140\text{--}2120\text{ cm}^{-1}$ (that is at the position characteristic of bands due to ketene ‘antisymmetric’ stretching vibrations) also appeared in the spectra of the irradiated matrix, showing that the ring-opening reaction did also occur for **mp5c**. However, taking into account the high absolute intensity of such modes [14] and the low intensity of the band at $2140\text{--}2120\text{ cm}^{-1}$ experimentally observed at all stages of the UV-induced process, one has to conclude that the aldehyde–ketene photoproduct is generated from **mp5c** only in very tiny amounts.

Noteworthy is the fact that no IR absorptions ascribable to the isomeric methyl 2-pyrone-3-carboxylate (**mp3c**) (Chart 1) could be found in the spectra recorded after UV irradiation of matrix-isolated **mp5c**. This shows that no process transforming **mp5** into **mp3c** occurred for matrix-isolated **mp5c** excited with UV light. Such a process would have to involve the sequence: ring-opening of **mp5c**, intramolecular hydrogen shift (such as that presented in Scheme 2) and ring-closure to **mp3c**. Because the ring-opening photoreactions in α -pyrones are photoreversible processes (they are always accompanied by ring-closure reactions), the missing step, which hinders the transformation of **mp5c** into **mp3c**, must concern the intramolecular hydrogen shift within the aldehyde–ketene structures.

In the present work, we have undertaken an investigation of the photochemical behaviour of methyl 2-pyrone-3-carboxylate (**mp3c**) isolated in low-temperature inert matrices. To the best of our knowledge, no studies on the photochemistry of **mp3c** have been reported hitherto. We shall demonstrate that, although **mp5c** is not photochemically transformed into **mp3c**, the photoconversion in the opposite direction (**mp3c** \rightarrow **mp5c**) is the dominant event in the photochemistry of **mp3c**.

2. Experimental and computational methods

A sample of methyl 2-pyrone-3-carboxylate (98%) used in the present study was a commercial product supplied by Aldrich. Argon of spectral purity 6.0 was supplied by Linde AG. To prepare a low-temperature matrix, solid sample of **mp3c** was electrically heated in a miniature glass oven placed in the vacuum chamber of a continuous-flow

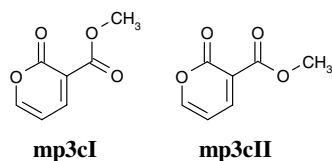


Chart 1. Relevant conformers of methyl 2-pyrone-3-carboxylate (**mp3c**) and their abbreviated names.

helium cryostat. Sublimation temperature of 2-pyrone-3-carboxylate was $55\text{ }^{\circ}\text{C}$. The vapours of the compound were deposited, together with ca. 1000-fold excess of argon, on a CsI window cooled to 10 K . The pressure of gaseous argon in the cryostat chamber was $3 \times 10^{-4}\text{ Pa}$ during the matrix deposition, whereas before and after the deposition this pressure was lower than 10^{-6} Pa . Argon deposition rate was ca. 1 mmol h^{-1} . The IR spectra were recorded with 0.5 cm^{-1} resolution using the Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector. Matrices were irradiated with light from HBO200 high-pressure mercury lamp fitted with a water filter and Schott WG295 or Schott UG11 cut-off filters transmitting light with $\lambda > 295\text{ nm}$ or $\lambda > 270\text{ nm}$, respectively. No evaporation or transformation of the matrix structure occurred during UV irradiation. Details concerning experiments with methyl 2-pyrone-5-carboxylate are provided in our previous Letter [14].

The geometries of the possible conformers of **mp3c** (as well as those of its putative photoproducts) were optimised using the density functional theory method with the B3LYP functional [15–17]. At the optimised geometries, the harmonic vibrational frequencies and infrared intensities were calculated. All quantum-mechanical calculations were performed with the GAUSSIAN 98 program [18] using the standard 6-311++G(d,p) basis set. To correct for the systematic shortcomings of the applied methodology (mainly for anharmonicity), the predicted vibrational wavenumbers were uniformly scaled by 0.978.

3. Results and discussion

The potential energy surface of **mp3c** was examined (using theoretical calculations carried out at the DFT(B3LYP)/6-311++G(d,p) level) for the presence of low-energy minima. Two such minima, corresponding to **mp3cI** and **mp3cII** structures presented in Chart 1, were localized.

The electronic energy (including the zero-point vibrational contribution) calculated (at the DFT(B3LYP)/6-311++G(d,p) level) for the **mp3cI** and **mp3cII** structures was higher by 19.4 and 25.6 kJ mol^{-1} (respectively) than the energy of **mp5cI** form calculated using the same method. The predicted energy gap between the more stable **mp3cI** and the less stable **mp3cII** forms (6.2 kJ mol^{-1}) increases slightly (to 6.7 kJ mol^{-1}) when the sublimation temperature of the compound during deposition of the matrix ($55\text{ }^{\circ}\text{C}$) and the calculated Gibbs free energies are taken into account. At $55\text{ }^{\circ}\text{C}$, the predicted populations of forms **mp3cI** and **mp3cII** in the gas phase are 92% and 8%, respectively. The energy barrier separating these forms was calculated to be higher than 13 kJ mol^{-1} in both directions. Such a barrier is high enough to preclude interconversions between the two conformers during their landing and cooling on the surface of an argon matrix at 10 K [19]. This implies that the relative populations of **mp3cI** and **mp3cII** conformers trapped in the matrix should be

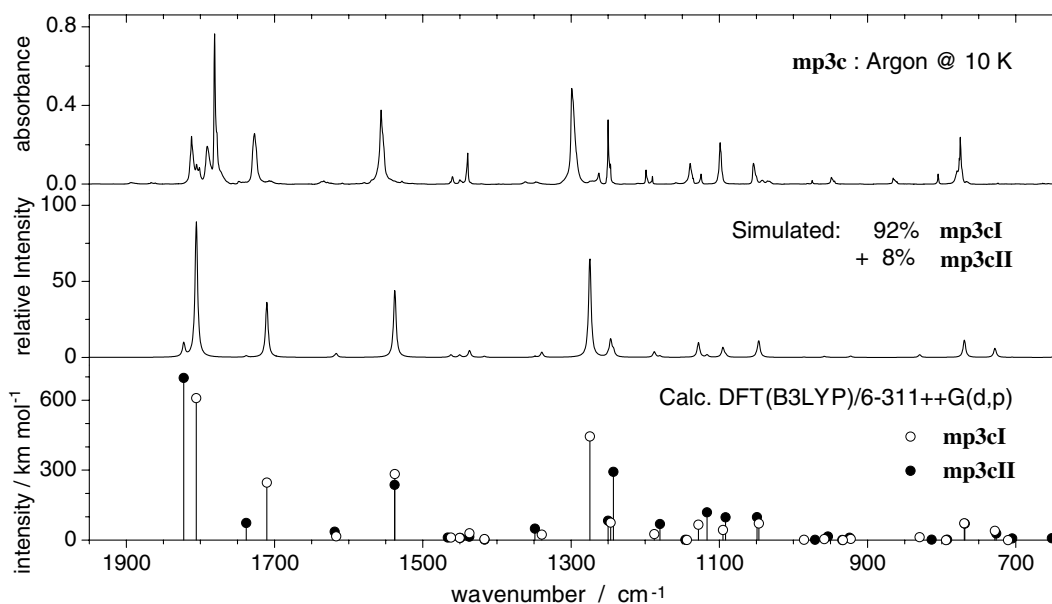


Fig. 2. Experimental FTIR spectrum of methyl 2-pyrone-3-carboxylate (**mp3c**) isolated in an Ar matrix at 10 K (top frame), compared with the infrared spectrum simulated for the gas-phase equilibrium mixture of conformers **mp3cI** and **mp3cII** (middle frame). The theoretical infrared spectra of individual conformers (bottom frame) were calculated at the DFT(B3LYP)/6-311++G(d,p) level of theory and frequencies were scaled by a factor of 0.978. Intensities in the stick spectra are not scaled. The sum spectrum was simulated using Lorentzian functions centered at the calculated (scaled) frequencies and with bandwidth-at-half-height equal to 4 cm^{-1} . Intensities of the calculated bands due to **mp3cI** and **mp3cII** conformers in the sum spectrum are population-weighted in accordance with their calculated Gibbs free energy difference (6.7 kJ mol^{-1}) at 55°C .

the same as they were in the gas phase prior to deposition [19].

The experimental IR spectrum of **mp3c** monomers isolated in an argon matrix is presented in Fig. 2 (upper frame). This spectrum is well reproduced by the spectrum simulated on the basis of the theoretical calculations carried out for **mp3cI** and **mp3cII** forms of the compound (middle frame). As it can be seen in Fig. 2 (bottom frame), the theoretical spectra of the two conformers of **mp3c** are very similar. However, it does not seem (see discussion below) that the exact knowledge concerning the conformational orientation of the methyl-ester group ($-\text{COOCH}_3$) is essential for the study of the photochemical transformations of **mp3c**.

During the course of UV ($\lambda > 295\text{ nm}$) irradiation of matrix-isolated **mp3c**, the IR bands belonging to the spectrum of the initial form of the compound were systematically and quite rapidly decreasing in intensity. Such behaviour concerned, e.g. the bands centered at 1812, 1791, 1781, 1727, 1139, 1125, 1099 and 1054 cm^{-1} , indicated by downward arrows in Fig. 3. Already after 15 min of irradiation, ca. 70% of the initially deposited **mp3c** was consumed, whereas after 1 h of irradiation nearly all of the starting compound was converted into other species (Figs. 3 and 4). Therefore, both **mp3cI** and **mp3cII** are consumed upon irradiation and the conformational multiplicity of **mp3c** is of minor importance from the viewpoint of the photochemical properties of the compound.

As far as the spectra of emerging photoproducts are concerned, one of the new eminent features is the band at

$2141/2132\text{ cm}^{-1}$ (Fig. 4). The frequency of this band is very characteristic of the ‘antisymmetric’ stretching vibration of the ketene group ($\text{C}=\text{C}=\text{O}$). Hence, appearance of the band at $2141/2132\text{ cm}^{-1}$ undoubtedly indicates that, upon exposure of the matrix to UV ($\lambda > 295\text{ nm}$) light, the aldehyde–ketene is photoproducted by opening of the **mp3c** ring. Comparison of Fig. 4, showing the progress of the phototransformations of **mp3c**, with the analogous photo-induced reactions of **mp5c** (Fig. 1), clearly demonstrates that the aldehyde–ketene photoproduct is generated in much higher amounts for the former compound. The aldehyde–ketene product photogenerated from **mp3c** can already be clearly observed after 15 min of UV irradiation (Fig. 4). Therefore, the aldehyde–ketene must be one of the species that are photogenerated first, without any ‘incubation’ time.

From the spectra presented in Fig. 4 (traces B, C and D), it is also evident that the shape of the band at ca. 2140 cm^{-1} changes in the course of UV irradiation of the matrix. One of the possible reasons for that can be the very high conformational flexibility of the open-ring aldehyde–ketene species. In the present study, the structures of 14 open-ring aldehyde–ketene conformers (all possible forms with the $\text{O}=\text{C}-\text{O}-\text{CH}_3$ axis in *cis* orientation) were optimised at the DFT(B3LYP)/6-31G(d,p) theory level. The geometry optimisations were then followed by calculations of the infrared spectra. The results of these calculations are available in the Supporting material (Fig. S1, Tables S1 and S2). For all these structures, the calculated frequencies of the antisymmetric $\text{C}=\text{C}=\text{O}$ stretching vibration fall into

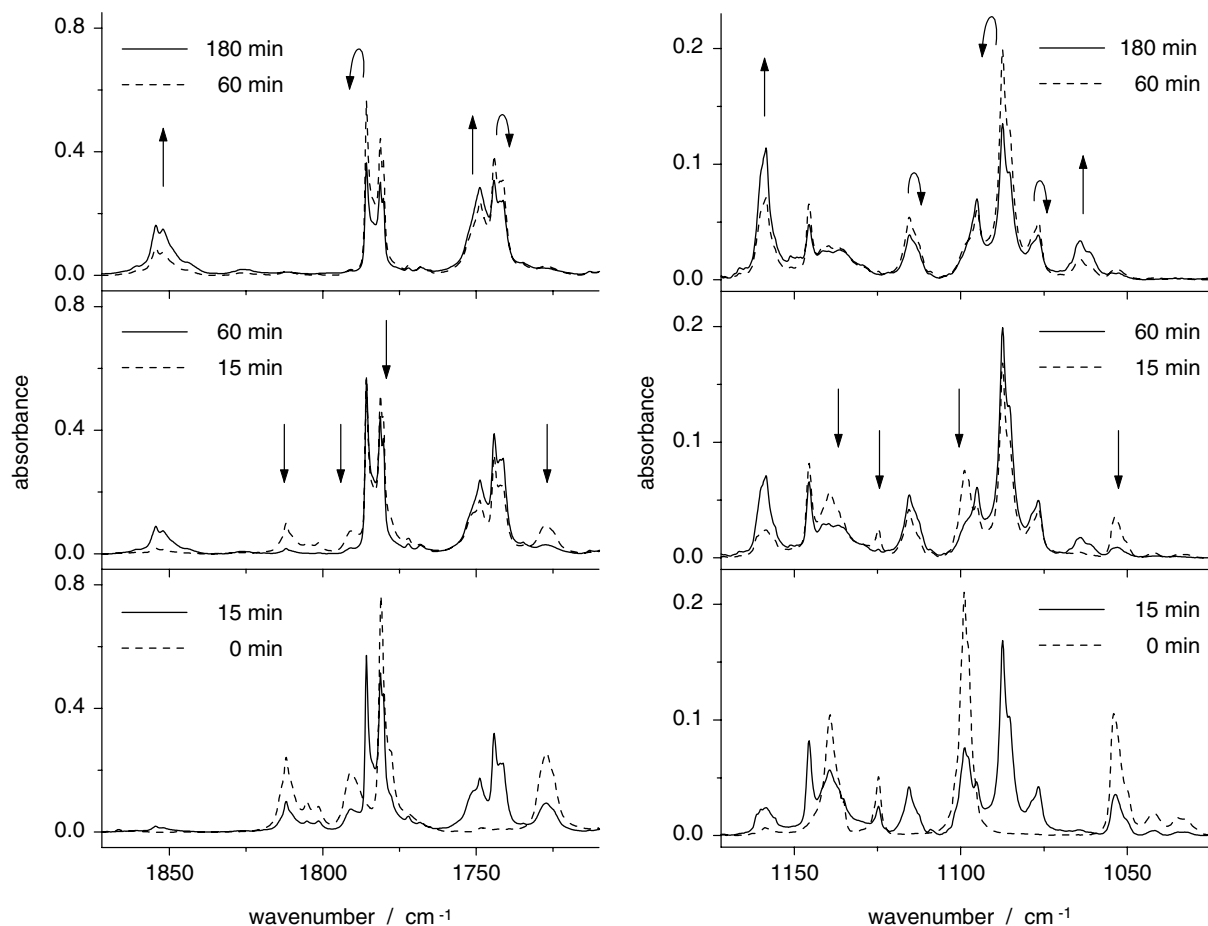


Fig. 3. Progress of photochemical changes induced by UV ($\lambda > 295$ nm) irradiation of methyl 2-pyrone-3-carboxylate (**mp3c**) isolated in an Ar matrix. The presented spectra were recorded before irradiation (0 min) and after 15, 60 and 180 min of irradiation. Arrows indicate three different patterns of changes during irradiation. The spectral regions are chosen so that bands exhibiting these three patterns of variation do not overlap significantly.

a narrow frequency range of $2211\text{--}2230\text{ cm}^{-1}$ (unscaled). This implies that the identification of individual conformers by comparison of the calculated and experimental spectra is impossible in practical terms.

Another reason that should be taken into account, when changes of the shape of the complex band at ca. 2140 cm^{-1} are considered, is the possibility of an intramolecular hydrogen shift of the type shown in Scheme 2. Would such hydrogen migration occur, then another family of aldehyde–ketene forms (those corresponding to open-ring **mp5c**) should appear in the matrix. However, we demonstrated [14] (Fig. 1) that for **mp5c** the photoequilibrium between the ring-opening and ring-closure processes (Schemes 1 and 4) is shifted very strongly in favour of the closed-ring **mp5c** structure. Hence, if the intramolecular hydrogen shift process does occur in the open-ring forms of **mp3c** (converting them into the open-ring forms of **mp5c**), one should expect accumulation of closed-ring **mp5c** species in the matrix.

Alongside the band at ca. 2140 cm^{-1} , another appealing IR spectral feature, emerging upon UV ($\lambda > 295$ nm) irradiation of matrix-isolated **mp3c**, is the absorption at 1852 cm^{-1} (Figs. 3 and 4). The very pronounced differences

in the kinetics of growth of the bands at $2141/2132\text{ cm}^{-1}$ and at 1852 cm^{-1} in the course of UV irradiation (Fig. 4) clearly show that the two bands indicate formation of two different photoproducts. The frequency of 1852 cm^{-1} is typical of the bands due to the stretching vibrations of C=O groups directly attached to small rings, such as the four-membered rings of the Dewar isomers. It is noteworthy that the band due to the Dewar isomer of **mp5c**, observed previously [14] in the experiments on UV irradiation of matrix-isolated **mp5c**, appeared exactly at the same frequency 1852 cm^{-1} (see also Fig. 1). An interesting feature characterizing the photogeneration of the Dewar isomer is the dependence of the intensity of the band at 1852 cm^{-1} on irradiation time. During the first 15 min of exposure of **mp3c** to UV ($\lambda > 295$ nm) light, more than a half (ca. 70%) of the population of the initial form of **mp3c** was consumed (see e.g. the intensities of the band at 1812 cm^{-1} in Figs. 3 and 4). But during this period only a very minor amount of the Dewar form was photogenerated. In the IR spectra recorded after 15 min of UV irradiation the band at 1852 cm^{-1} is only barely visible (Fig. 4 trace B). This band reaches a notable intensity no sooner than after 1 h of irradiation (Fig. 4 trace C). Moreover,

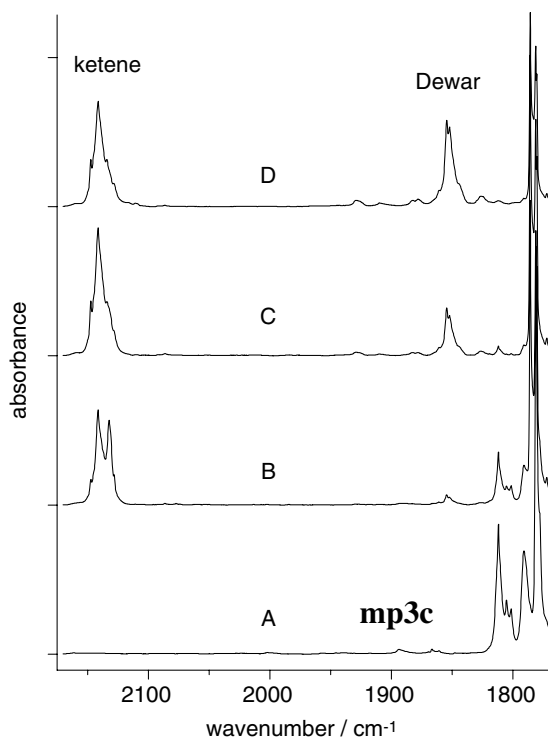


Fig. 4. Progress of photochemical changes induced by UV ($\lambda > 295$ nm) irradiation of methyl 2-pyrone-3-carboxylate (**mp3c**) isolated in an Ar matrix at 10 K. The spectra were recorded: (A) before irradiation, (B) after 15 min, (C) after 60 min and (D) after 180 min of irradiation.

at the beginning of the last period of irradiation there was only a very little amount of the unreacted **mp3c** (see the band at 1812 cm^{-1} in trace C of Fig. 4), which could serve as a substrate of a photoreaction. Nevertheless, during this last period, a significant amount of the Dewar form was photogenerated (see the band at 1852 cm^{-1} in traces C and D of Fig. 4). Summarizing, it is quite obvious that the amount of the Dewar product, generated during a certain period of the observed photoprocess, is (drastically) not proportional to the amount of the initial form of **mp3c** consumed during the same period. At the initial stages of UV irradiation of **mp3c** there is a clear ‘incubation’ period, when the photogeneration of the Dewar form is very small, though the initial compound is substantially consumed. The photogeneration of the Dewar isomer is, however, much more pronounced at the final stages of the photoinduced process, when the consumption of the initial **mp3c** substrate is negligible. These observations unequivocally indicate that the Dewar isomer is not formed directly from **mp3c**. They also strongly suggest that there must be an intermediate (or a chain of intermediates) which is/are produced from the initial **mp3c** substrate, but then is/are consumed in the reaction generating the Dewar isomer.

Analysis of the sequence of IR spectra, recorded at consecutive stages of the UV-induced transformations of **mp3c** (Fig. 3), led to identification of a set of bands which first appear and grow, but then decrease in intensity in the course of irradiation of the matrix. These bands (marked with

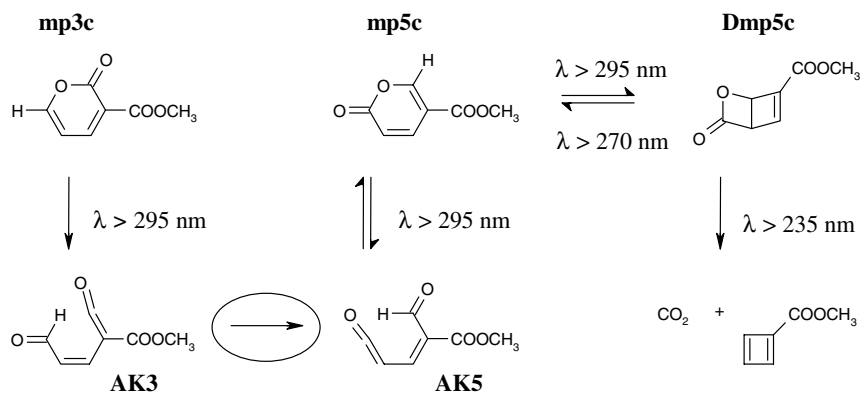
curved arrows in Fig. 3) indicate photogeneration and subsequent consumption of a species that could serve as a candidate for the intermediate in production of the Dewar form. Fortunately, the identification of this species was a very straightforward task. On the basis of our previous experiments [14], it was easy to note that the spectral positions of the bands, exhibiting the same pattern of intensity variation (growth followed by decrease) during the time of UV irradiation, coincide with the positions of IR bands constituting the spectrum of **mp5c** isolated in an argon matrix.

Also the more specific identification of the chemical structure of the Dewar form, generated as one of the final products in the experiments (carried out in the present work) on UV irradiation of matrix-isolated **mp3c**, turned out to be feasible. A set of IR bands (such as, e.g. those at 1159 and 1064 cm^{-1} , marked with upward arrows in Fig. 3), which share the same pattern of intensity changes (monotonic buildup) with the absorption at 1852 cm^{-1} , was found to nicely coincide with the spectrum of the Dewar isomer of **mp5c**.

The latter form (**Dmpc5**, see Scheme 6) was found in our previous Letter [14] to be the major photoproduct generated upon UV ($\lambda > 295$ nm) irradiation of matrix-isolated **mp5c**. We demonstrated [14] that the phototransformation of **mp5c** into its Dewar isomer **Dmp5c** is photoreversible and that this photoreaction leads to the photostationary state, where both **mp5c** and **Dmp5c** are present in a photoequilibrium. Also the phototransformations occurring upon UV ($\lambda > 295$ nm) irradiation of the matrix-isolated **mp3c** (studied in the present work) lead to a state where the final products are **mp5c** and **Dmp5c**, whereas the initial form of **mp3c** is totally consumed. The spectrum recorded after prolonged irradiation of a matrix, which initially contained monomers of **mp3c**, coincides well (see traces C and D in Fig. 5) with the superposition of the spectra of **mp5c** and **Dmp5c** derived from the previous experiments [14] on the photochemistry of matrix-isolated methyl 2-pyrone-5-carboxylate.

Slight differences in shapes of the corresponding bands in traces C and D of Fig. 5 could be explained by relative populations of rotamers **Dmp5cI** and **Dmp5cII** as well as **mp5cI** and **mp5cII**, which do not necessarily need to be the same in experiments having **mp3c** or **mp5c** as the initially deposited species. Nevertheless, the picture presented in Fig. 5 is very convincing and leaves no doubt about identification of **mp5c** and **Dmp5c** as the final products of UV ($\lambda > 295$ nm) induced phototransformations of matrix-isolated monomers of **mp3c**.

On the basis of the knowledge accumulated in the past (see Section 1) and concerning the UV-induced apparent shifts of substituents round the pyran ring of α -pyrone derivatives, a mechanism of phototransformation of **mp3c** into **mp5c** can be proposed. This mechanism (presented in Scheme 6) involves: (1) opening of the **mp3c** ring, (2) hydrogen shift within open-ring aldehyde–ketenes leading to transformation of **AK3** into **AK5** and (3) ring-closure of **AK5** to the closed-ring product **mp5c**.



Scheme 6. UV-induced photochemical changes experimentally observed for monomeric **mp3c** and **mp5c** isolated in low-temperature (10 K) Ar matrices. The uni-directional character of the intramolecular hydrogen shift is indicated by the arrow in oval. The migrating hydrogen atom is shown explicitly.

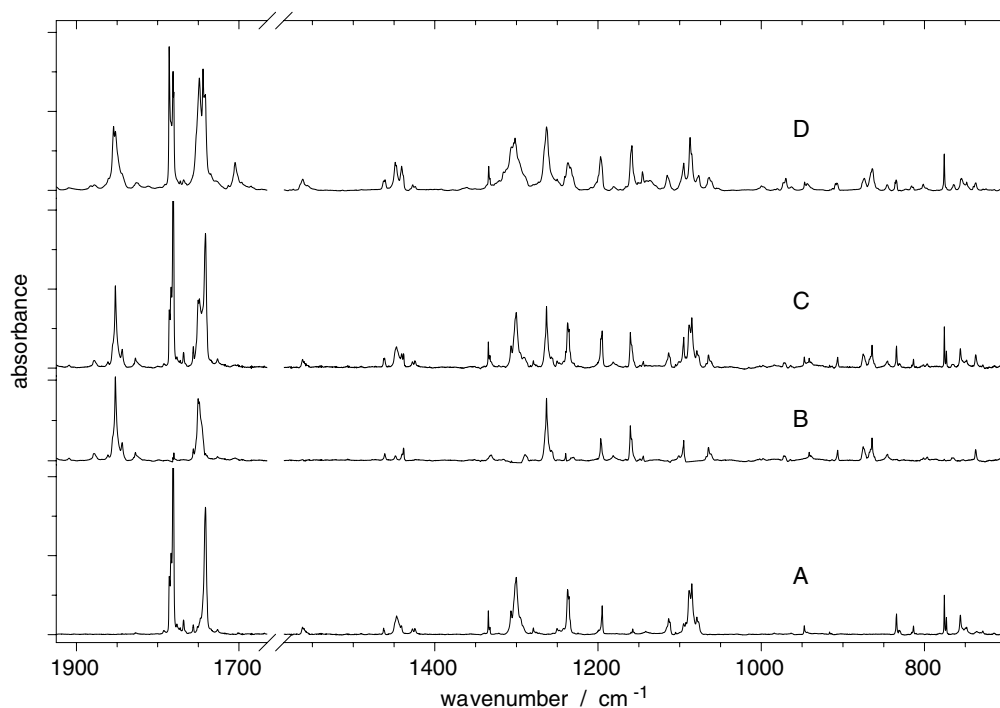


Fig. 5. (A) Experimental FTIR spectrum of **mp5c** monomers isolated in a freshly deposited low-temperature Ar matrix at 10 K (see Fig. 1d in Ref. [14]); (B) spectrum of the Dewar isomer of **mp5c**, generated upon UV ($\lambda > 295 \text{ nm}$) irradiation of **mp5c** (see Fig. 3c in Ref. [14]); (C) sum of spectra A and B and (D) spectrum recorded after 180 min of UV ($\lambda > 295 \text{ nm}$) irradiation of **mp3c** isolated in an Ar matrix.

Other photoreactions shown in Scheme 6: (a) photo-transformation of **mp5c** into its Dewar isomer **Dmp5c** (occurring upon UV ($\lambda > 295 \text{ nm}$) irradiation) and (b) generation of an antiaromatic methyl-ester cyclobutadiene by decarboxylation (upon UV ($\lambda > 235 \text{ nm}$) irradiation) of **Dmp5c**, are known from the previous Letter [14] on the photochemistry of **mp5c**.

There are several possible reasons which could preclude transformation of **mp3c** into **Dmp3c**. The first of such reasons is related with the steric properties of the Dewar isomers. Comparison with the phototransformation of **mp5c** into **Dmp5c** is particularly relevant, because for the initial forms (**mp3c** and **mp5c**) as well as for the Dewar forms

(**Dmp3c** and **Dmp5c**) the substituent (methylcarboxy group) is the same, only its position in the molecule is different. Both conformers of the starting compound have a planar (**mp3cI**) or approximately planar (**mp3cII**) arrangement of the heavy atoms (see Fig. 1). Planar arrangement of heavy atoms is also characteristic of both conformers of **mp5c**. In such a case, the studied molecules can fit easily between layers of a closely-packed argon crystal, substituting a few argon atoms. This situation is very likely to occur during the deposition of a matrix sample. Once a matrix is deposited and cooled to 10 K, the solid argon becomes rigid and keeps the planar geometry of the matrix cage corresponding to the shape of the studied molecule. The

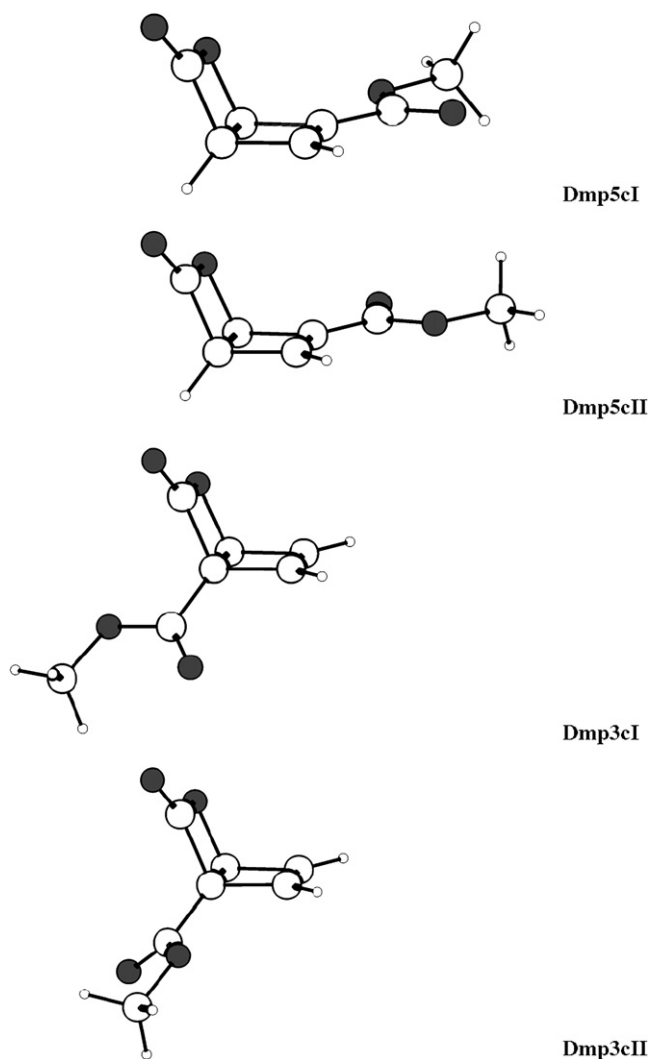


Fig. 6. 3-D views of Dewar isomers of methyl 2-pyrone-5-carboxylate and methyl 2-pyrone-3-carboxylate optimised at the DFT(B3LYP)/6-311++G(d,p) level of theory in vacuum. Note the same orientation of the Dewar fragment for all structures. Oxygen atoms are greyed.

optimized geometries of Dewar isomers, both for the 5-substituted and the 3-substituted compounds, are presented in Fig. 6.

The structures presented in Fig. 6 are characteristic of the Dewar isomers in vacuum. If such structures are to be formed in rigid low-temperature matrices, then it is obvious that the Dewar isomer formed from the 5-substituted compound would require only small rearrangement of the matrix cage, whereas for **Dmp3c** the necessary rearrangements of the cage must be substantial. In the structure of **Dmp5c** Dewar form, only the O=C–O sub-unit deviates from the plane containing all other heavy atoms. In the 3-substituted Dewar isomer, in addition to the O=C–O sub-unit, the ring substituent (–COOCH₃) undergoes a strong reorientation too (see Fig. 6). Thus, in comparison to the phototransformation of **mp5c** into **Dmp5c**, photogeneration of **Dmp3c** from **mp3c** should require much stronger distortion of the matrix cage. The alternative reac-

tion pathway (ring-opening) results in formation of a completely planar structure **AK3** (Scheme 6), the shape of which resembles very closely that of the starting compound (geometry of the optimized structure is depicted in the Supporting material), and would require only a minor readjustment of the rigid argon environment.

Besides the steric effects, also the electronic properties of **mp3c** can be responsible for suppression of the UV-induced isomerization of **mp3c** into **Dmp3c**. It has been proposed that the photochemical channel, leading in α -pyrones to contraction of their planar, six-membered rings to the Dewar forms, involves an excited state with dominant $\pi\pi^*$ character [20]. On the other hand, cleavage of the α -bond and generation of open-ring ketene products is a photoprocess that originates from an excited state with $n\pi^*$ character [21]. For several substituted α -pyrones, it was experimentally demonstrated that the two lowest-energy excited states have $n\pi^*$ and $\pi\pi^*$ characters [20]. It was also shown that the (usually small) energy gap between these two excited states, is a sensitive function of substituents attached to the ring [22]. Hence, interactions between a substituent and the α -pyrone ring through the π -system shall be particularly relevant in conditioning the dominance of one of the types of the photochemical reactions typical of the compound. In turn, these interactions can be expected to be highly sensitive to the position occupied by the substituent. These expectations are in agreement with the experimental results showing quite a different photochemical behaviour of **mp3c** and **mp5c**.

4. Conclusions

Summarizing the UV-induced photochemical behaviour of **mp3c**, it must necessarily be stressed that the primary photochemical transformation of this compound is the ring-opening reaction leading to formation of the aldehyde–ketene photoproduct. This transformation is not only primary, but it is also dominating and practically the unique photochemical reaction of **mp3c**. The ring-opening photoreaction is then followed by an intramolecular hydrogen shift, which is in fact responsible for the migration of the –COOCH₃ substituent from position 3 to position 5 of the pyran ring. This key event for the whole scheme of phototransformations of **mp3c** is marked in Scheme 6 by an arrow enclosed in oval. Once **mp5c** is formed (in a subsequent ring-closure reaction), then it undergoes photochemical transformations typical of this compound [14]. These UV-induced changes result mostly in the formation of the Dewar isomer **Dmp5c**.

The matrix-isolation studies on photochemical reactions of both **mp3c** and **mp5c** lead to conclusion that transformation of **mp3c** into **mp5c** is uni-directional. Two sets of observations support strongly this conclusion. Firstly, UV ($\lambda > 295$ nm) irradiation of **mp3c** resulted (at the end of the reaction) in total consumption of the initial form of this compound, though (at this stage) there was a significant amount of photoproduct **mp5c** accumulated in the

matrix. This would be impossible if a non-negligible photoprocess converting **mp5c** into **mp3c** existed. Secondly, in the experiments on UV ($\lambda > 295$ nm) irradiation of **mp5c**, no traces of IR bands, characteristic of **mp3c** (e.g. that at 1812 cm^{-1}), appeared at any stage of the photoprocess (see Fig. 1).

Comparison of the present study on **mp3c** and the previous investigation of **mp5c** demonstrates a very different photochemical behaviour exhibited by these two isomeric derivatives of α -pyrone. Whereas the photochemistry of **mp5c** is strongly dominated by the effective, photoreversible transformation of the compound into its Dewar isomer, the UV-induced changes in **mp3c** concern exclusively the ring-opening, α -bond cleavage reaction followed by an intramolecular hydrogen atom transfer. This illustrates well that not only the nature of substituent, but also its position at the pyran ring defines the dominating channel of photoinduced transformations of α -pyrones.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2007.12.027.

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