Mechanism of the Photochemical Isomerization of Indan-Dions to Benzylidenephthalides

I. Timtcheva and P. Nikolov
Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

J. Zechner and N. Getoff
Institute of Theoretical Chemistry and Radiation Chemistry, The University of Vienna, Wien, Austria

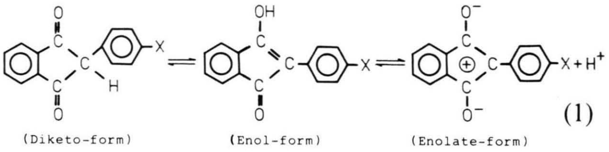
St. Minchev
University of Shumen, 9700 Shumen, Bulgaria

Z. Naturforsch. **42 a,** 490–494 (1987); received January 23, 1987

The photoinduced isomerization of 15 2-arylindan-1,3-diones and 5 2,6-diaryl-s-hydrindacene-1,3,5,7-tetrones was studied. Spectroscopic data, quantum yields of final products and a probable processes of these compounds are presented.

1. Introduction

The photochemical isomerization of 2,2-diaryl- and 2,2-dialkylindan-1,3-diones to the corresponding 3,3-diaryl- and 3,3-dialkylmethylene-1 (3H)-isobenzofuranones (benzilidenephthalines) has been described by Rigaudy and Derible [1–3]. In contrast to these compounds, which have a fixed diketo-structure, the 2-phenylindan-1,3-dione and its derivatives, substituted in p-position of the phenyl ring, can exist in two tautomeric forms, depending on the polarity of the solvent [4]. These are the diketo-form (structure K), which predominates in aprotic nonpolar solvents (cyclohexane, heptane etc.) and the enol-form (structure E), prevailing in polar protic solvents (e.g. methanol, ethanol). In alkaline water ($pH = 12$) these compounds are present in the enolate form.



(1)

The photochemical behaviour of several 2-arylindan-1,3-diones in solvents of different polarity has been previously described [5–8]. The obtained results illustrate that photoisomerization of the starting compounds to the corresponding benzylidenephthalides takes place in all cases. The highest yields of the photoproducts were obtained in cyclohexane, where the diketoform predominates. This fact suggests that probably the diketo-form of indan-diones is responsible for the photochemical isomerization to benzylidene-phthalides.

The aim of the present investigations was to elucidate the mechanism of the photochemical isomerization of indan-diones and to answer the question, which tautomeric form is responsible for this photoreaction.

2. Experimental

The investigated compounds (see Table 1) were synthesized by standard procedures [10–20] and were recrystallized until a constant melting point was obtained. Their purity was controlled by thin-layer chromatography.

The solvents used were of fluorescence or reagent grade.

The flash photolysis experiments were performed independently on two equipments: a) Flash kinetic spectrophotometer, KN 100 (Applied Photophysics, London) and b) modified apparatus "Nothern Precision" as described in [5].

The fluorescence spectra were recorded on a Perkin-Elmer MPF 44B Spectrofluorimeter and the absorptions spectra on a Specord M40 (Carl Zeiss, Jena, DDR) or on a Hitachi 115-20 spectrophotometer. For the steady photochemical experiments a medium pressure mercury lamp (Tungsram HGO 125 W) was used.

Reprint requests to Prof. Dr. N. Getoff, Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, Währingerstr. 38, A-1090 Wien, Austria.

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The quantum yield of the photochemical isomerization of 2-arylindan-1,3-diones was determined using an apparatus for monochromatic irradiation, coupled with a quantum counter (Applied Photophysics Ltd., London).

3. Results and Discussion

Detailed investigations were performed with respect to the photochemical behaviour of 2-arylindan-1,3-diones, substituted in p-position of the phenyl ring. In order to avoid the influence of some factors (e. g. the keto-enol tautomerism), the photochemical properties of compounds with similar structure, e. g. 2,6-diaryl-s-hyrindacene-1,3-5,7-tetrones (bis-indandiones), substituted in p,p′-position of the phenyl ring [7, 8] and 2-aminosubstituted-2-arylindan-1,3-diones [9] were studied. It is known [4] that the 2-arylindan-1,3-diones can exist in two tautomeric forms, depending on the solvent polarity. In nonpolar solvents (e. g. cyclohexane) the diketo-form predominates, where the % ratio $K:E$ according to [4] is 94:6. In polar protic solvents like ethanol, the enol-form prevails (the % ratio $K:E = 44:56$ [4]). In water at $p\mathrm{H} = 12$ the equilibrium is strongly shifted to the anion-form. Consequently in all cases an equilibrium between these three tautomeric forms is present.

In order to discuss the influence of monochromatic irradiation on the photochemical behaviour of the tautomeric forms of 2-arylindan-1,3-diones, first an analysis of their individual absorption bands is made.

The absorption spectra of 2-p-aminophenylindan-1,3-dione in cyclohexane, ethanol and water at $p\mathrm{H} = 12$ are shown in Figure 1.

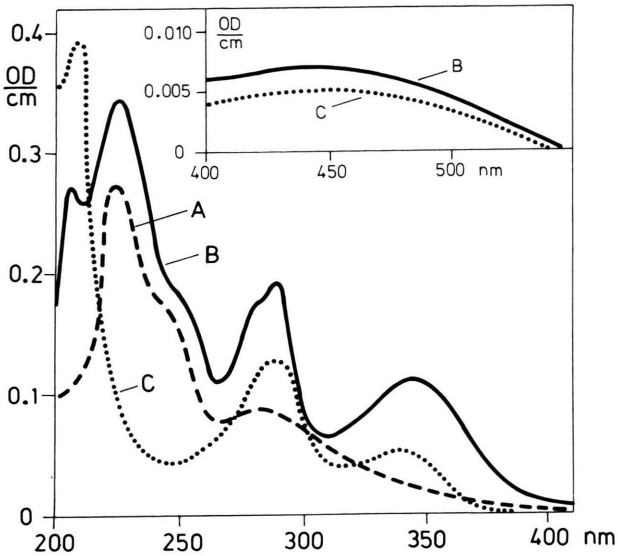


Fig. 1. Absorption spectra of 10^{-5} mol · dm^{-3} 2-p-aminophenylindan-1,3-dione in cyclohexane (diketo-form of the substrate; A), in ethanol (mainly enol-form; B) and in water at $p\mathrm{H} = 12$ (enol-form only; C). – *Insert:* Continuation of the spectra B and C in the range of 400 to 600 nm.

The band at 225 nm ($\varepsilon_{225} = 2.75 \times 10^4$ dm^3 mol^{-1} cm^{-1}) of spectrum A with shoulder around 250 nm is due to absorption of the diketo-form, as it is missing in water at $p\mathrm{H} = 12$, where the equilibrium is strongly shifted to the anion-form. The same holds for the band at 280 nm ($\varepsilon_{280} = 9 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in cyclohexane which corresponds to the absorption of o-phthalaldehyde. The absorptions maximum at 210 nm (spectrum B in Fig. 1) results from alocal excitation in the phenyl ring, and at 290 nm ($\varepsilon_{290} = 1.9 \times 10^4$ dm^3 mol^{-1} cm^{-1}) is due to excitation in the substituted phenyl ring, its position being strongly dependent on the nature of the substituent in p-position. The same is valid for spectrum C. Further absorption bands of the enol and anion forms are at 345 nm ($\varepsilon_{345} = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}; spectrum B) and at 340 nm ($\varepsilon_{340} = 5 \times 10^3$ dm^3 mol^{-1} cm^{-1}; spectrum C) in addition to the absorption at about 430–450 nm (Fig. 1, insert).

For comparison also the absorption spectra of 2-p-methoxyphenylindan-1,3-dione (A) and of p-methoxybenzyliden-phthalide (B) with their spectroscopic characteristics are given in Figure 2.

The experimental results, which can be related to the mechanism of the photochemical isomerization of indan-diones to benzylidene-phthalides can be summarized as follows:

1. The flash and steady state u. v.-irradiation of 2-arylindan-1,3-diones in cyclohexane, ethanol and water at $p\mathrm{H} = 12$ leads in all cases to a photochemical isomerization to benzylidene-phthalides. The yields of these products, calculated from the intensity of their absorption maxima for solutions of equal concentration (1×10^{-4} mol · dm^{-3}), are highest in cyclohexane ($\sim 0.8 \times 10^{-6}$ mol · dm^{-3}), where the diketo-form predominates. In ethanol, where the keto-enol equilibrium is shifted to the enol-form, the yields of formation of benzylidene-

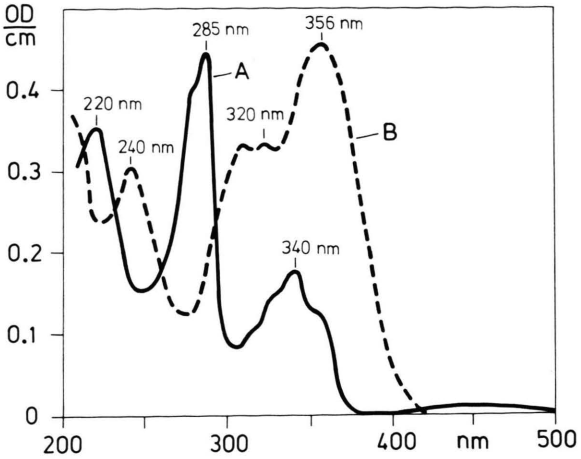


Fig. 2. Absorption spectrum of 2.4×10^{-5} mol · dm^{-3} 2-p-methoxy-phenylindan-1,3-dione (A) and of $2 \cdot 10^{-5}$ mol dm^{-3} p-methoxybenzyliden-phthalide (B) in ethanol. Spectroscopic characteristics of:

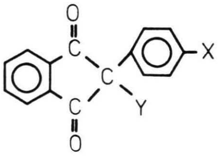
A		B	
λ_{max} (nm)	ε (dm^3 mol^{-1} cm,$^{-1}$)	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})
220	1.47×10^4	240	1.53×10^4
285	1.85×10^4	320	1.64×10^4
340	7.40×10^3	365	2.26×10^4

phthalides are lower (~ 0.5×10^{-6} mol · dm^{-3}). In water at $pH = 12$, where indan-diones exist almost only in the anion form, traces of benzylidenephthalides were formed only from indandiones with electron-donating substituents in p-position of the phenyl ring.

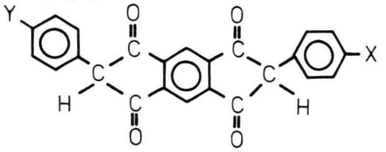
2. The quantum yields of the photochemical isomerization (Q) of 2-phenylindan-1,3-dione in cyclohexane and of 2-p-methoxy-phenalindan-1,3-dione in ethanol were determined. The highest quantum yield in cyclohexane was observed after monochromatic irradiation at 254 nm ($Q = 7.98 \times 10^{-2}$), which corresponds to irradiation at the absorption maximum of the diketo-form, and the lowest ($Q = 6.35 \times 10^{-4}$) after irradiation at the maximum of the enol-form) (366 nm). Similar results were observed in ethanol, with highest $Q = 9.0 \times 10^{-3}$ at 220 nm (the maximum of the diketo-form) and lowest $Q = 9.0 \times 10^{-5}$ at 340 nm (the maximum of the enol-form (Figure 2). The fact that the irradiation in the maximum of the enol-form leads to the formation of a photo-product, even with a very low yield, can easily be explained, having in mind that the diketo-form also absorbs in this spectral region.

Table 1. List of the investigated substances of type A and B.

A) 2-arylindan-1,3-diones:



B) 2,6-diaryl-s-hydrindacene-1,3,5,7-tetrones:



Substitute groups on the positions:

A-type Nr.	X	Y	B-type Nr.	X	Y
1	$-N(CH_3)_2$	$-H$	1	$-H$	$-H$
2	$-NH_2$	$-H$	2	$-CH_3$	$-CH_3$
3	$-NHCOCH_3$	$-H$	3	$-OCH_3$	$-OCH_3$
4	$-OCH_3$	$-H$	4	$-H$	$-OCH_3$
5	$-CH_3$	$-H$	5	$-CH_3$	$-OCH_3$
6	$-F$	$-H$			
7	$-Cl$	$-H$			
8	$-H$	$-H$			
9	$-CN$	$-H$			
10	$-Br$	$-H$			
11	$-H$	$-Br$			
12	$-H$	$-NH_2$			
13	$-H$	$-NHCH_2C_6H_5$			
14	$-H$	$-NHC_2H_5$			
15	$-H$	$-N(CH_3)_2$			

Table 2. Quantum yield (Q) of photochemical isomerization of $5 \cdot 10^{-4}$ mol dm^{-3} 2-phenylindan-1,3-dione in cyclohexane to benzylidene-phthalide.

Irrad. at (nm):	Q
254	7.98×10^{-2}
265	4.62×10^{-2}
313	6.4×10^{-3}
366	6.35×10^{-4}

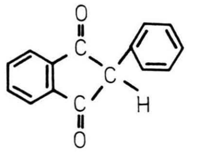
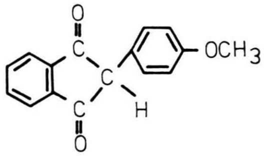

(2-phenylindan-1,3-dione)

Table 3. Quantum yields (Q) of the photochemical isomerization of $1 \cdot 10^{-4}$ mol dm^{-3} 2-p-methoxyphenylindan-1,3-dione in ethanol to benzylidene-phthalide.

Irrad. at (nm):	Q
220	9.0×10^{-3}
280	2.1×10^{-3}
340	9.0×10^{-5}


(2-p-methoxy-phenylindan-1,3-dione)

The determined quantum yields in cyclohexane and ethanol are shown in Tables 2 and 3.

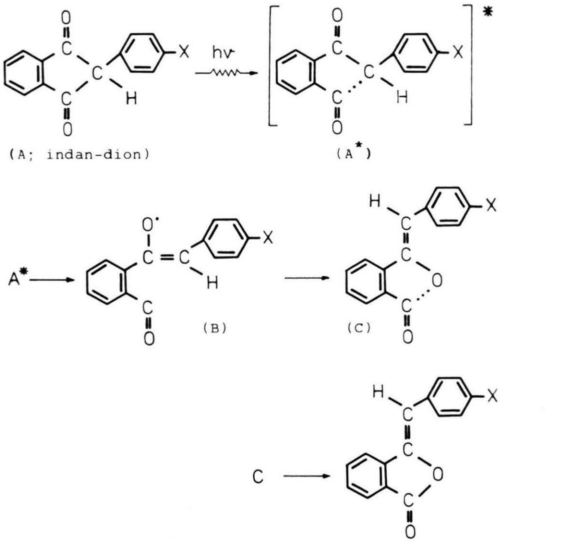
3. On monochromatic irradiation of solutions of 2-phenylindan-1,3-dione and 2,6-diphenyl-s-hydrindacine-1,3,5,7-tetrone (bis-indandione) in the long wavelength absorption maxima of the enolform (435 and 520 nm respectively), the diketo-form does not lead to the formation of benzylidene-phthalide or bis-benzylidenephthalide (the absorption spectra of the starting compounds remain unchanged).

4. The compound with fixed enol-form, namely 3-methoxy-2-phenyl-2-inden-1-one, is photostable. Both 2-bromo-2-phenylindan-1,2-dione and 2-amino-2-phenylindan-1,3-dione, which exist solely in diketo-form, give upon irradiation the corresponding benzylidene-phthalides. As an example, the transient absorption spectrum obtained by flash photolysis of 2-bromo-2-phenylindan-1,3-dione in dichloroethane as well as the spectrum of the resulting final product is presented in Figure 3.

The experimental results show that, most probably, the photoreaction of indan-diones to benzylidene-phthalides goes through their diketo-tautomeric form.

This hypothesis is well supported by the experimental results for the photochemical rearrangements of 2,6-diaryl-s-hydrindacene-1,3,5,7-tetrones (bis-indan-diones). They can exist in two tautomeric forms also, but in contrast to 2-arylindan-1,3-diones, the equilibrium is strongly shifted to the enol-form even in aprotic solvents of low polarity, e.g. dichloroethane. The staedy state and flash u.v.-irradiation of bis-indan-diones in ethanol (where they exist almost in the enol form) does not lead to the formation of the corresponding bis-benzylidene-phthalides. In dichloroethane (diketo-form of the substrate) a photoisomerization of bis-indan-diones to bis-benzylidene-phthalides was observed.

Taking into account all the experimental results, one could conclude that the photoisomerization of indan-diones to benzylidene-phthalides goes through the following reaction mechanism:



(D; benzylidene-phthalide)

This mechanism is known in the literature [21–25] as a Norrish type I reaction of splitting of the C–C bond in the α-position to a carbonyl group, which is typical for carbonyl compounds. All the investigated compounds are β-diketones, and the obtained experimental results concerning their photochemical rearrangements could be explained assuming a Norrish type I mechanism only.

Acknowledgements

The authors greatly appreciate the financial support given by the Austrian Federal Ministry for Science and Research and of the Bulgarian Academy of Sciences, which made this cooperation possible.

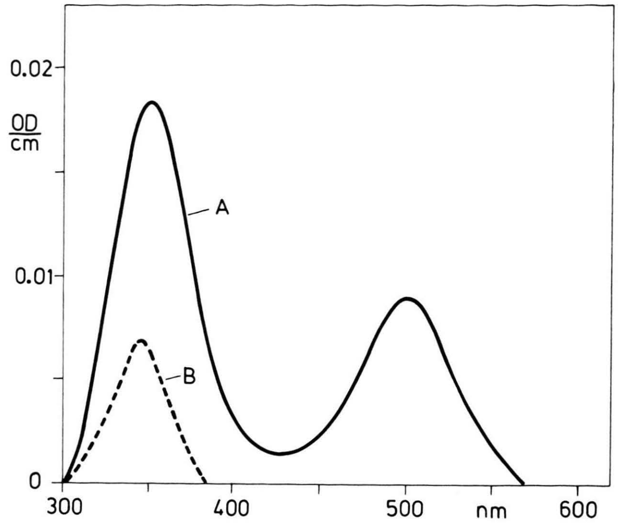


Fig. 3. Absorption spectrum of the transients resulting from 5×10^{-5} mol dm^{-3} 2-bromo-2-phenylindan-1,3-dione in dichloroethane (A) and of the final product (B).

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