Photochemical Properties of 2-Aryl-3-imino-1-indones

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Steady state as well as flash photolysis experiments of 2-aryl-3-imino-1-indones (2-AIID) have been carried out with the aim to learn more about their photochemical properties. It was established that in ethanol these substances exist solely in the keto-enamine-form and are rather photostable under the influence of uv-light. Illumination in dichloroethane, acetonitrile and dioxane is leading to stable photoproducts. A typical transient absorption spectrum of 2-AIID is presented. Probable reaction mechanisms are given.

1. Introduction

The photochemical properties of some carbonyl organic compounds belonging to the group of indian-diones and bis-indian-diones namely 2-arylindan-1,3-diones and 2,6-diaryl-s-hydrindacen-1,3,5,7-tetrones have been studied in solvents of different polarity [1–3]. It has been shown that upon UV-light irradiation of these compounds two parallel photochemical reactions take place: photoisomerization to stable end products (benzylidene-phthalides and bis-benzylidene-phthalides) as well as formation of transients (2-aryl-indandionyl radicals and bis-indandionyl radicals).

2-Aryl-indan-diones and bis-indan-diones can exist in two tautomeric forms, the keto- and enol one, of which the equilibrium can be shifted to one of them, depending on the solvent polarity [1, 2].

A detailed investigation of the mechanism of the photoinduced isomerization of indian-diones and bis-indadiones to benzylidene-phthalides and bis-benzyl-idene-phthalides showed [3] that the photochemical transformation proceeds via the keto form.

Based on these data concerning the indan-dione compounds, it was now of special interest to investigate the 2-aryl-3-imino-1-indone substances in the same respect. These dyestuffs differ from the indandiones by the replacement of one of the keto-groups by an imino group. The experiments were primarily focused on the change of the photochemical properties of these substances under the influence of light. Some studies of the photoinduced formation and decay of the corresponding transients by means of flash-photolysis are also mentioned in this work. The compounds under investigation are also of interest being efficient luminophores in their cristal phase [4].

2. Experimental

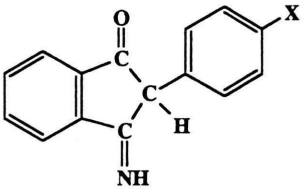
The investigated dyestuffs (see Table 1) were synthesized by a standard procedure [5] and recrystallized until a constant melting point was obtained. Their purity was controlled by thin-layer chromatography.

All solvents (Merck, Darmstadt) were of spectroscopic or reagent grade and have been distilled under Argon before use.

The concentration of the solutions, irradiated under steady state conditions, was in the range 5×10^{-4} to 5×10^{-5} mol dm^{-3}.

The flash-photolysis experiments were performed with a modified apparatus "Northern Precision" as previously described [1]. For the steady-state photochemical experiments a medium pressure mercury

Table 1. List of the investigated compounds.



Comp. Nr.	X
1	$-H$
2	$-CH_3$
3	$-OCH_3$
4	$-N(CH_3)$
5	$-F$

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lamp (Tungsram HGO 125 W) was used. The solutions were illuminated in a quarz vessel at a distance of 50 cm from the lamp.

The absorbtion spectra were taken on a Hitachi 115-20 spectrophotometer.

The fluorescence spectra were recorded by means of a Perkin-Elmer MPF-44 B spectrofluorimeter.

The substances needed for comparison (e.g. phthalimides) have been synthesized and purified before use.

3. Results and Discussion

3.1. Steady-State Experiments

2-Aryl-3-imino-1-indones (2-AIID) can exist in three tautomeric forms [6]: keto-imine (I), keto-enamine (II) and enol (III) ones (Figure 1).

It was previously shown [6] on the basis of comparison with the model compounds IV, V and VI (Fig. 2) that in polar protic solvents (methanol, ethanol) the equilibrium between the above mentioned three tautomeric forms is entirely shifted to the keto-enamine form (II).

Freimanis and Vanag [6, 7] have studied in detail the UV absorption spectra of 2-aryl-3-imino-1-indones and found that in all used solvents (alcohols, ethers, hydrocarbons) the spectra have bands around 225 nm, 280 nm 300–320 and about 450 nm (Figure 3). The longest wave-length transmission, which is responsible for the red colour of the studied compounds in solution, is connected with the conjugated N–C=C–C=O system and consequently with the keto-enamine tautomeric form II [6].

As already mentioned, 2-aryl-3-imino-1-indones in ethanol exist solely in the keto-enamine-form (II) (Fig. 1), which is an analog of the enol-form of 2-arylindiandiones. The solutions of 2-aryl-3-imino-1-indones in ethanol are photostable upon steady-state as well as flashed light, and their absorption spectra remain unchanged even after 60 min irradiation with light (Tungsram HGO 125 W). Consequently, a photochemical transformation of 2-aryl-3-imino-1-indones to stable products via the keto-enamine-form (II) is impossible.

However, the steady-state irradiation of 2-aryl-3-imino-1-indones in dichloroethane, acetonitrile and dioxane is leading to the formation of a stable product. This fact is illustrated by the change of the absorption spectra in dichloroethane upon UV-irradiation (Figure 4).

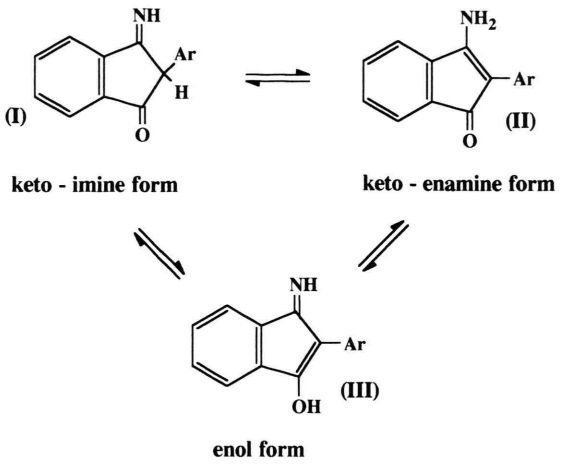

Fig. 1. Tautomeric forms of 2-aryl-3-imino-1-indones.

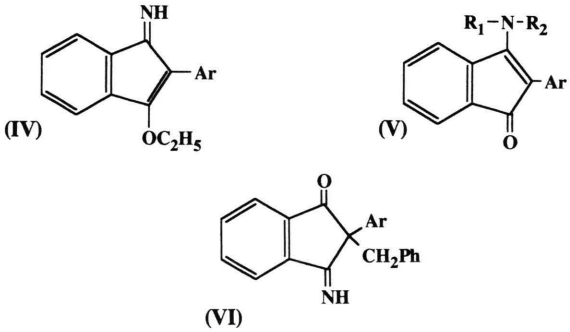

Fig. 2. Model compounds used for the investigations.

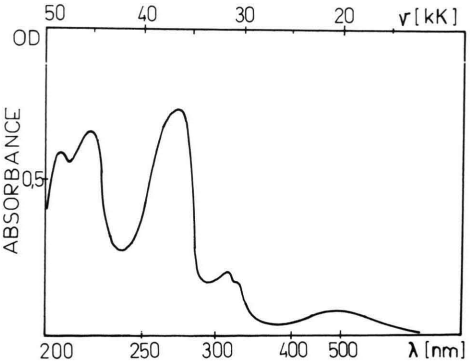

Fig. 3. Absorption spectrum of 1×10^{-5} mol dm^{-3} 2-(p-OCH_3-phenyl)-3-imino-1-indone in ethanol.

Most probably the reason for this photoinduced transformation is the presence of the keto-imine-form (I) of 2-AIID, which is a structural analog of the diketo-form of 2-arylindan-diones. This conclusion is similar to the ones achieved in the previous investigations [3], where it has been shown that the diketo-form of 2-

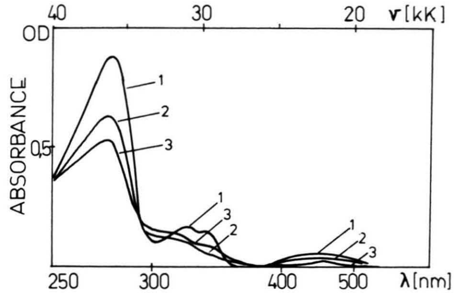

Fig. 4. Light induced changes of the absorption spectrum of 1×10^{-5} mol dm^{-3} 2-(p-OCH_3-phenyl)-3-imino-1-indone in dichloroethane measured at: 0 min (1), 15 min (2) and 30 min (3) in the presence of air (see text).

arylindan-1,3-diones is responsible for their photochemical isomerization to benzylidene-phthalides. The photoproduct resulting from steady-state irradiation of the investigated 2-AIID is formed with highest yield in dichloroethane. Table 2 shows the spectral characteristics of the stable photoproducts (see later).

Upon UV-irradiation the carbonyl compounds of the indan-dione types photoisomerize via a Norrish type II reaction [8–11]. In the case of 2-aryl-3-imino-1-indones there are two possible routes of photochemical isomerization (Norrish type II) depending on which bond is initially ruptured: the simple C–C bond next to the imino-group (Fig. 5 A) or next to the

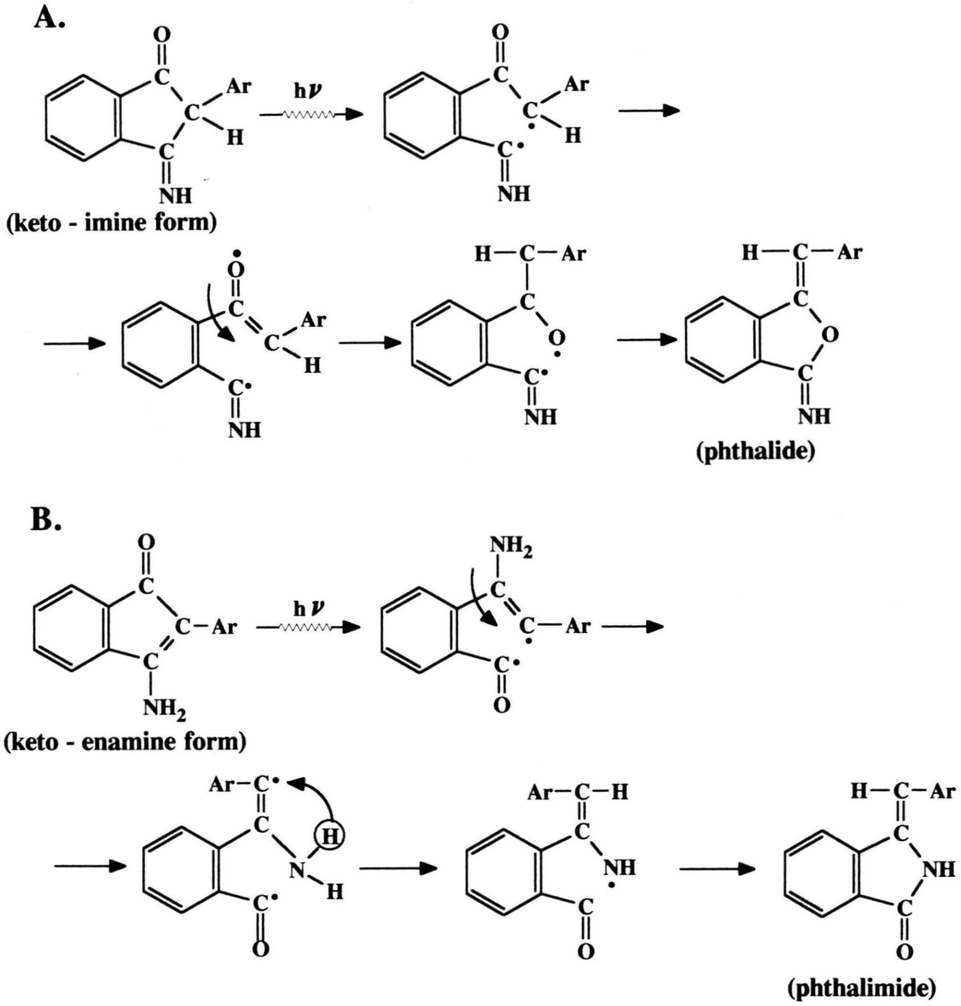

Fig. 5 Possible path of the photochemical isomerization of 2-aryl-3-imino-1-indones.

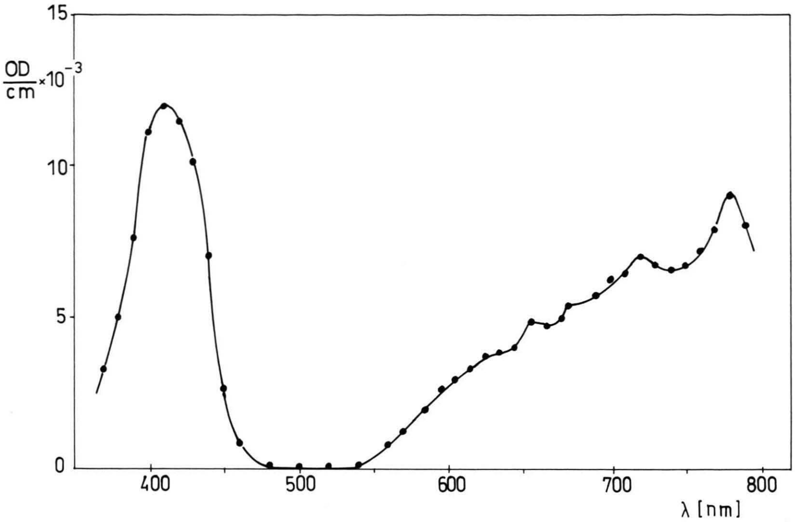

Fig. 6. Transient absorption spectrum observed by flash photolysis of deoxigenated 3×10^{-5} mol dm^{-3} 2-(p-dimethylamino-phenyl)-3-imino-1-indone in dichloroethane at 500 μs after flash; discharge voltage 8 kV.

Table 2. Absorption (λ_{abs}) and fluorescence (λ_{fl}) maxima (nm) of the stable end products resulting from the investigated compounds observed in dichloroethane, acetonitrile and dioxane.

Nr.	Dichloroethane			Acetonitrile			Dioxane		
	λ_{abs}	λ_{ex}	λ_{fl}	λ_{abs}	λ_{ex}	λ_{fl}	λ_{abs}	λ_{ex}	λ_{fl}
1	358	370	455	365	370	450	352	360	420
2	354	370	435	353	360	490	359	–	–
3	366	360	450	367	370	445	360	370	430
4	374	370	435	370	370	430	378	380	510
5	346	360	430	365	370	450	351	360	420

carbonyl group (Figure 5 B). In the former case (5 A) the starting compound is in its keto-imine form and the expected end product is a phthalide (like in the case of 2-aryl-indandiones); in the latter case (5 B) the starting compound is in the keto-enamine form and the expected end product is a phthalimide.

The experimental data from the steady-state irradiation of the studied 2-AIID in solution show that the photoinduced reaction proceeds according to the mechanism given in Fig. 5 A and that the stable product is phthalide. This conclusion is based on the following facts:

- The absorption and fluorescence characteristics of the photoproducts in dichloroethane, acetonitrile and dioxane (Table 2) are practically identical with those of the benzylidene-phthalides described in [12].
- In ethanol, where practically only the keto-enamine-form of 2-aryl-3-imino-1-indones is present [6] and the Norrish II reaction is expected to follow the scheme given in Fig. 5 B, no photochemical transformation leading to a stable product is observed.
- Freimanis and Vanag [6] have shown that only the keto-enamine form (II) of the 2-AIID in solution is responsible for the absorption band in the region of 450 nm. The illumination of this compound in dichloroethane, acetonitrile and dioxane in the presence of air with monochromatic light (λ = 450 nm) does not lead to any changes of the absorption spectra. Hence, no stable photoproducts were formed under these experimental conditions.

3.2. *Flash-photolysis Experiments*

Flash-photolysis experiments of 2-AIID compounds in dichloroethane were also performed. All studied compounds, with exception of p-F-2-aryl-3-imino-1-indone (Table 1, No. 5) form transients with absorption bands in the range 350 to 450 nm (Figure 6). The maxima of the transients are very close in position to those of the corresponding 2-aryl-indandionyl-radicals previously reported [1].

On the basis of this fact it may be assumed that upon flash-photolysis of 2-AIID the H-atom in position 2 splits off, resulting in 2-aryl-3-imino-indanoyl radicals.

Only in the case of $-N(CH_3)_2$ substituted 2-AIID (Table 1, No. 4) the transient absorption spectrum shows an additional band in the region of 600–800 nm (Figure 6).

Acknowledgements

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