PHOTOCHEMICAL ISOMERIZATIONS OF 2-PHENYL-1,3-INDANEDIONE TO *E*- AND *Z*-BENZALPHTHALIDE AND OF *E*-BENZALPHTHALIDE TO *Z*-BENZALPHTHALIDE

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The photochemical isomerizations have been studied of 2-phenyl-1,3-indanedione to mixture of *E*- and *Z*-benzalphthalide and of *E*-benzalphthalide to *Z*-benzalphthalide depending on the solvent used, concentration, and the light wavelength. The attempts at the reverse photochemical isomerization of *E*-benzalphthalide to 2-phenyl-1,3-indanedione have failed. Quantum yields of the isomerization of 2-phenyl-1,3-indanedione decrease in the following solvent series: cyclohexane > acetonitrile ≃ benzene > tetrachloromethane ≫ methanol. The isomerization quantum yield of 2-phenyl-1,3-indanedione is inversely proportional to concentration of the starting substance, but the dependence of $1/\Phi$ on the concentration is not linear.

Classical methods of preparation of *E*-benzalphthalides, *viz.* the Gabriel modification of the Perkin synthesis as well as the Ogliar method result in formation of practically pure *E*-isomers[1], although the phthalides isolated from natural materials have both *E* and *Z* configurations. Rigaudy and Derible showed in their papers[2,3] that 2-phenyl-1,3-indanedione can be isomerized photochemically to mixture of *E*- and *Z*-benzalphthalides and *vice versa.*

The aim of our work was a detailed study of the photochemical isomerization of 2-phenyl-1,3-indanedione to the mixture of *E*- and *Z*-benzalphthalides, of the reverse isomerization of benzalphthalide to 2-phenyl-1,3-indanedione as well as that of *E*-benzalphthalide to *Z*-benzalphthalide. Our purpose was to suggest the reaction mechanism on the basis of study of the solvent effects, concentration dependences, and influence of wavelength of the light used on the quantum yield of the isomerization reactions.

EXPERIMENTAL

The quantum yields were measured with an apparatus consisting of a high-pressure mercury discharge lamp Osram HBO 200 or a medium-pressure discharge lamp RVI 125 working in medium-pressure or low-pressure regimes, a monochromator with high output of light beam in UV region (Applied Photophysics), a temperating block, a beam divider, photo-electric cells, integrator, and magnetic stirrer (Fig. 1).

The substance was irradiated in an 1 × 1 cm quartz cell. With the use of a calibration curve (potassium ferric oxalate) for the given wavelength we determined the absolute light intensity impinging on the cell with the reaction mixture. The samples were degasified three times at 0·014 Pa.

The quantum yields obtained in repeated measurements differed less than by 10%.

The preparative photochemical reactions were carried out in a photochemical reactor with a quartz finger. The light of the high-pressure mercury discharge lamp was filtered through simax glass, the resulting emission spectrum is given in Fig. 2.

The UV spectra were measured with a UV VIS NIR PE 450 spectrophotometer, the IR spectra with a PE 180 spectrophotometer, and the ^1H NMR spectra were measured at 80 MHz with a Tesla BS 487 apparatus.

The solvents used: Benzene for UV, purified on a SiO_2 column of 1 cm diameter and 1 m length. Cyclohexane *p.a.* purified and dried[4]. Tetrachloromethane for IR spectroscopy. Acetonitrile (Cambrian Chemicals) purified[5]. Methanol for UV.

The starting 2-phenyl-1,3-indanedione was prepared according to ref.[6].

Preparation of E- *and* Z-*benzalphthalides.* 400 mg 2-phenyl-1,3-indanedione in 400 ml benzene for UV was irradiated in the photochemical reactor with glass filter for 3 h, nitrogen gas being bubbled through the reaction mixture for the whole time. Thereafter the solvent was evaporated, and the substance was submitted to column chromatography (SiO_2 L 100/250 for chromatography, Lachema, Brno; cyclohexane–chloroform 4 : 1). *E*-Benzalphthalide was eluted as the first fraction followed by the *Z*-isomer. The *E*- and *Z*-benzalphthalides were identified by IR, UV, and ^1H NMR spectra. *E*-Benzalphthalide: IR (CCl_4, cm^{-1}): $\nu_{C=O}$ 1 797, $\nu_{C=C}$ 1 662; ^1H NMR ($CDCl_3$, ppm): 6·15 (1 H, m, —CH=). *Z*-Benzalphthalide: IR (CCl_4, cm^{-1}): $\nu_{C=O}$ 1 789, $\nu_{C=C}$ 1 657; ^1H NMR ($CDCl_3$, ppm): 6·65 (1 H, m, —CH=); m.p. 95—97°C (ref.[7] m.p. 97°C).

From the other solvents we did not isolate *E*- and *Z*-benzalphthalide, but we determined the photostationary state by means of ^1H NMR spectra.

RESULTS AND DISCUSSION

The photolysis of 2-phenyl-1,3-indanedione in cyclohexane gave a mixture of *E*- and *Z*-benzalphthalide with the ratio 8·8 : 1, which is similar to results of refs[2,3]. On the other hand, our attempts at photochemical isomerization of *E*-benzal-

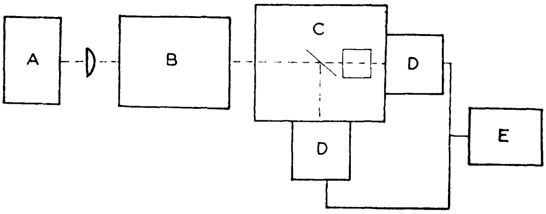


FIG. 1

Schematic representation of the apparatus used for the measurements of quantum yields. **A** HBO 200, **B** monochromator, **C** the temperating block, **D** photo-electric cell, **E** integrator phthalide to 2-phenyl-1,3-indanedione failed. With benzalphthalide the only reaction observed in the photolysis at the 366 or 340 nm wavelength was the isomerization of the starting substance to *Z*-benzalphthalide, which is contradictory to results of refs[2,3]. No reaction of *E*-benzalphthalide was observed in photolytic experiments at 254 nm wavelength in the same solvent.

We suppose that the different photochemical behaviour of 2-phenyl-1,3-indanedione is due to the different type of the lowest excited state of the two compounds (Fig. 3). In the case of 2-phenyl-1,3-indanedione the $n-\pi^*$ band is well separated from the first $\pi-\pi^*$ band (Fig. 4) thanks to large energy difference between the two states. Therefore, it seems likely that its lowest excited state has the $T_1(n-\pi^*)$ nature. The vacancy in the *n*-orbital of this excited state enables then the Norrish splitting I and the subsequent isomerization of biradical and formation of benzalphthalides. In the case of *E*-benzalphthalide the $n-\pi^*$ absorption band is completely overlapped by the $\pi-\pi^*$ band, and the $T_1(\pi-\pi^*)$ state represents the lowest excited state, which results in the α-splitting. This hypothesis is supported by the fact that 2-phenyl-1,3-indanedione isomerizes to *E*- and *Z*-benzalphthalide in cyclohexane at the 366 and 254 nm wavelengths. *E*-Benzalphthalide isomerizes to *Z*-benzalphthalide in cyclo-

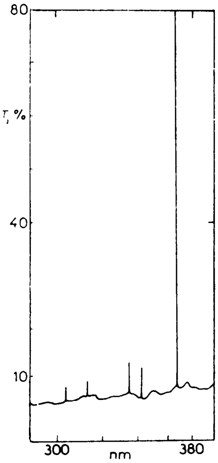


FIG. 2

The emission spectrum of the 400 W high-pressure mercury discharge lamp with glass filter

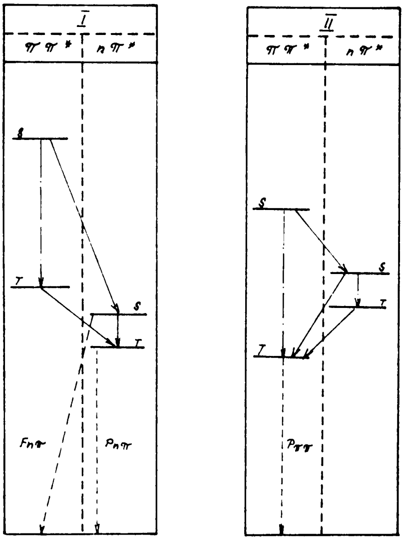


FIG. 3

The energy diagrams for 2-phenyl-1,3-indanedione (*I*) and benzalphthalide (*II*) hexane at the 366 nm wavelength, but 2-phenyl-1,3-indanedione is not formed, and at the 254 nm wavelength neither *Z*-benzalphthalide nor 2-phenyl-1,3-indanedione is formed. Addition of naphthalene to solution of 2-phenyl-1,3-indanedione in cyclohexane before irradiation at 366 nm wavelength results in a large decrease of the isomerization quantum yield ($\Phi_{\text{with naphthalene}} = 0{\cdot}011$, $\Phi_{\text{without naphthalene}} = 0{\cdot}11$). This is due to quenching of the $T(n-\pi^*)$ state of 2-phenyl-1,3-indanedione by naphthalene (254·8 kJ mol^{-1}). On the contrary, addition of naphthalene to solution of *E*-benzalphthalide in cyclohexane before irradiation at the 254 nm wavelength causes a sensitized isomerization to Z-benzalphthalide. An equilibrium is established between 62·9% *E*-isomer and 37·1% Z-isomer. In the former case naphthalene quenches the excited state, whereas in the latter case it sensitizes the given reaction.

Also the non-linear dependence of photochemical transformation of 2-phenyl-1,3-indanedione to benzalphthalide (Fig. 5), $1/\Phi$ *vs* concentration of 2-phenyl-1,3-indanedione supports the mentioned hypothesis, because it indicates that the quenching concerns more than one excited state.

We found that the quantum yields of photoisomerization of 2-phenyl-1,3-indanedione decrease with increasing concentration (Table I). The dependence of this yield on the concentration of the starting substance is caused by the fact that in-

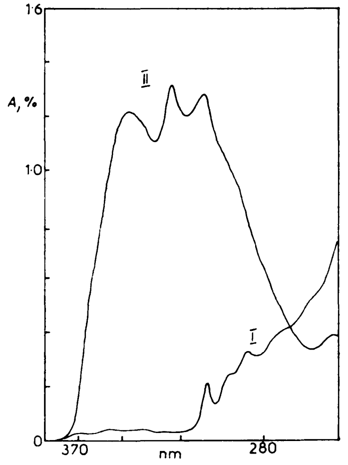


FIG. 4

UV Spectra of *E*-benzalphthalide (*II*) and 2-phenyl-1,3-indanedione (*I*) ($c_{\text{E-benzalphthalide}} = 1 \,.\, 10^{-4}$, $c_{\text{indanedione}} = 1 \,.\, 10^{-3}$ mol l^{-1}, 0·5 cm cell, cyclohexane)

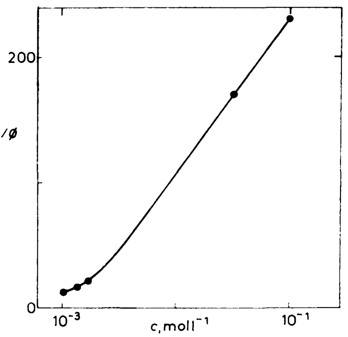
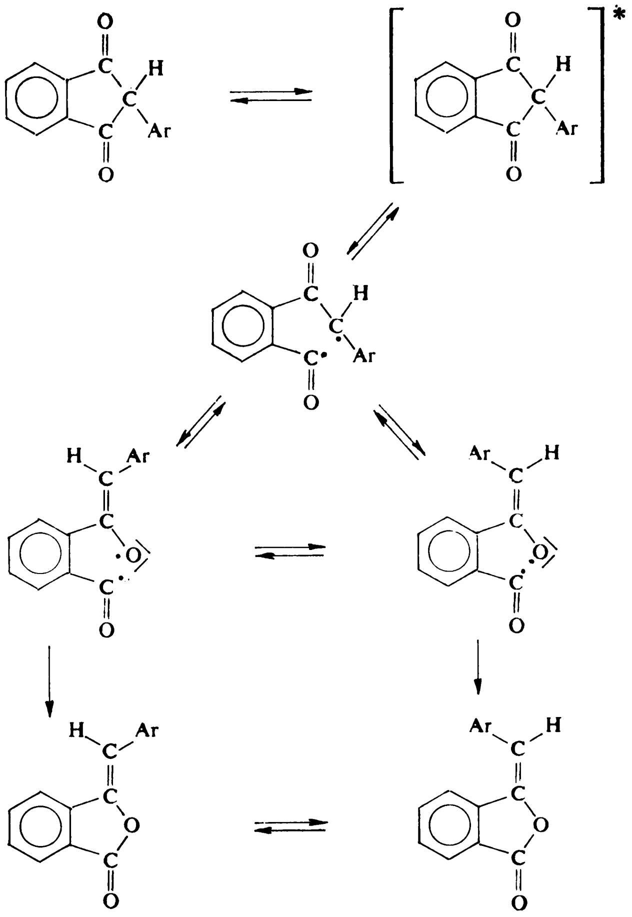


FIG. 5

Dependence of $1/\Phi$ *vs* concentration of 2-phenyl-1,3-indanedione



SCHEME 1

creasing concentration of the starting substance results in increasing concentration of the exciplex formed by the 2-phenyl-1,3-indanedione molecule in its ground and excited states[8] Scheme 1. By means of this exciplex there occurs a self-quenching of the excited state.

We measured the quantum yields of isomerization of 2-phenyl-1,3-indanedione depending on the wavelength of the radiation used. The wavelengths λ(nm) = 366, 340, 313, 254 were chosen to be close to the absorption maxima of the starting substance. The results in Table II show that the highest quantum yield of direct photolysis was obtained at the 366 nm wavelength and a still higher at 254 nm which is, however, a sensitized reaction. The results indicate that the reaction can take place from the short-living (τ . 10^{-11} s) singlet state, or the intercombination conversion $S \rightarrow T$ proceeds faster than the establishing of the equilibrium $S_0 \rightarrow S_n$.

The electronic spectra of 2-phenyl-1,3-indanedione and *E*-benzalphthalide are overlapped in the wavelength regions in which the dependence of the quantum yield *vs* wavelength was studied, which results in changes of I_a (intensity of the absorbed light) at the individual wavelengths.

The quantum yield of the photochemical transformation of 2-phenyl-1,3-indanedione into the benzalphthalide mixture was found to be a function of intensity of the absorbed light (I_a). (I_{01} = 3·3 . 10^{13} quanta/s ml, Φ_1 = 0·005, Φ_{02} = 6·5 . 10^{13} quanta/s ml, Φ_2 = 0·015, I_{03} = 3·0 . 10^{14} quanta/s ml, Φ_3 = 0·060). Even the dependence itself of Φ *vs* I_a can cause a dependence of quantum yield of the photoreaction on the wavelength, hence it is impossible to draw unambiguous conclusions from the mentioned relation.

When studying the dependence of the isomerization course of 2-phenyl-1,3-indanedione on the solvent used, we found that solvent not only affects the isomerization

TABLE I

Concentration dependence of quantum yield of photoisomerization of 2-phenyl-1,3-indanedione

No	Solvent	λ nm	Φ	C mol/l
1	UV benzene	366	0·077	1 . 10^{-3}
2	UV benzene	366	0·060	2 . 10^{-3}
3	UV benzene	366	0·049	3 . 10^{-3}
4	UV benzene	366	0·006	5 . 10^{-2}
5	UV benzene	366	0·004	1 . 10^{-1}

TABLE II

Dependence of quantum yield of photoisomerization of 2-phenyl-1,3-indanedione on wavelength

No	Solvent	λ nm	Φ	C mol/l
1	UV benzene	366	0·060	2 . 10^{-3}
2	UV benzene	340	0·010	2 . 10^{-3}
3	UV benzene	313	0·016	2 . 10^{-3}
4	UV benzene	254	0·113	2 . 10^{-3}

quantum yield (Table III) but also the yield of the benzalphthalide mixture and the ratio of the two isomers (Table IV). The highest yield (in %) was observed when the reaction was carried out in acetonitrile and tetrachloromethane, and the highest proportion of *Z*-benzalphthalide was obtained in benzene for UV. The quantum yields decrease in the series: cyclohexane > acetonitrile ≃ benzene > tetrachloromethane ≫ methanol. The individual solvents differ in their effects on the energy of the ground and excited states of the starting substance, which finally results in a decrease and increase, respectively, of quenching ability of the 2-phenyl-1,3-indanedione molecule in the ground state Scheme 2. These results agree with the observed efficiency in self-quenching of the triplet states of benzophenones[9,10] and other carbonyl compounds[11-13]. The distinct decrease in the quantum yield as well as percentage

TABLE III

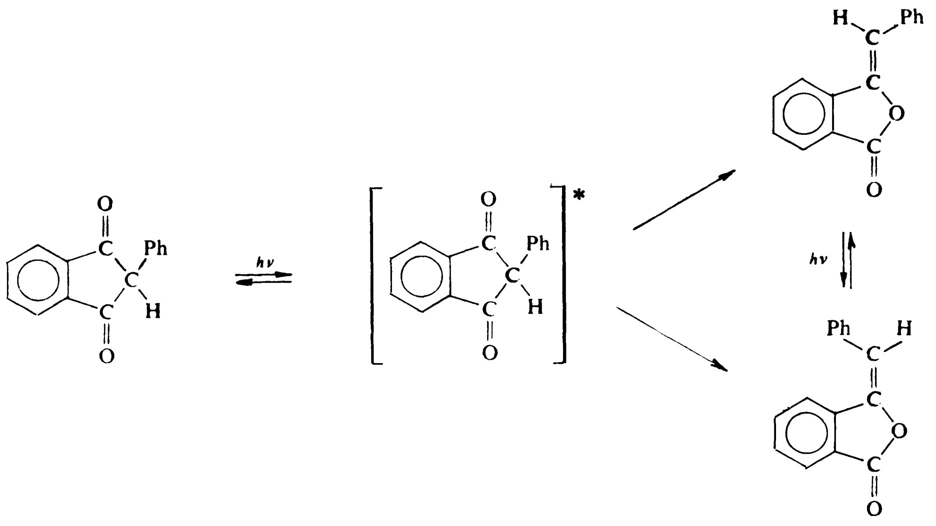
Solvent dependence of quantum yield of photoisomerization of 2-phenyl-1,3-indanedione

No	Solvent	λ nm	Φ	C mol/l
1	benzene	366	0·060	$2 . 10^{-3}$
2	cyclohexane	366	0·105	$2 . 10^{-3}$
3	CCl_4	366	0·049	$2 . 10^{-3}$
4	CH_3CN	366	0·064	$2 . 10^{-3}$
5	CH_3OH	366	0·018	$2 . 10^{-3}$
6	CH_3OH	436	0	$2 . 10^{-3}$

TABLE IV

Solvent dependence of the photoisomerization yield of 2-phenyl-1,3-indanedione and *E* : *Z* ratio of the benzalphthalide isomers

No	Solvent	λ nm	Benzalphthalide		Total yield %
			E-isomer, %	*Z*-isomer, %	
1	UV benzene	254	20	15·4	35·4
2	UV benzene	366	66·3	23·8	90·1
3	CH_3CN	366	86·5	6·7	93·2
4	CH_3OH	366	47·1	0	47·1
5	CCl_4	366	86·5	3·0	89·5
6	cyclohexane	366	72·2	8·2	90·4



SCHEME 2

yield of benzalphthalide in methanol deserve special attention. As a protic solvent methanol supports formation of associates of ketoenol form of 2-phenyl-1,3-indanedione, which increases self-quenching, and its high solvation ability also decreases the $\pi-\pi^*$ transition energy and, at the same time, hinders the rotation which is a condition of the rearrangement.

From our results it follows that the photochemical isomerization of 2-phenyl-1,3-indanedione can be expressed schematically.

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