

Photochemical isomerization of 2-alkyl-2-phenyl-1,3-indanediones to *E*- and *Z*-disubstituted methylenephthalides

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Photochemical isomerization of 2-R-2-phenyl-1,3-indanediones (R = C₆H₅CH₂, CH₃CH₂, CH₃) to corresponding *E*- and *Z*-isomers of disubstituted methylenephthalides revealed that the nature of R affects both the proportion of *E*- and *Z*-isomers of phthalides and the yield of isomerization, but has no significant influence on quantum yields. Attempted isomerization of the formed phthalides to the parent derivatives of 1,3-indanedione met with failure.

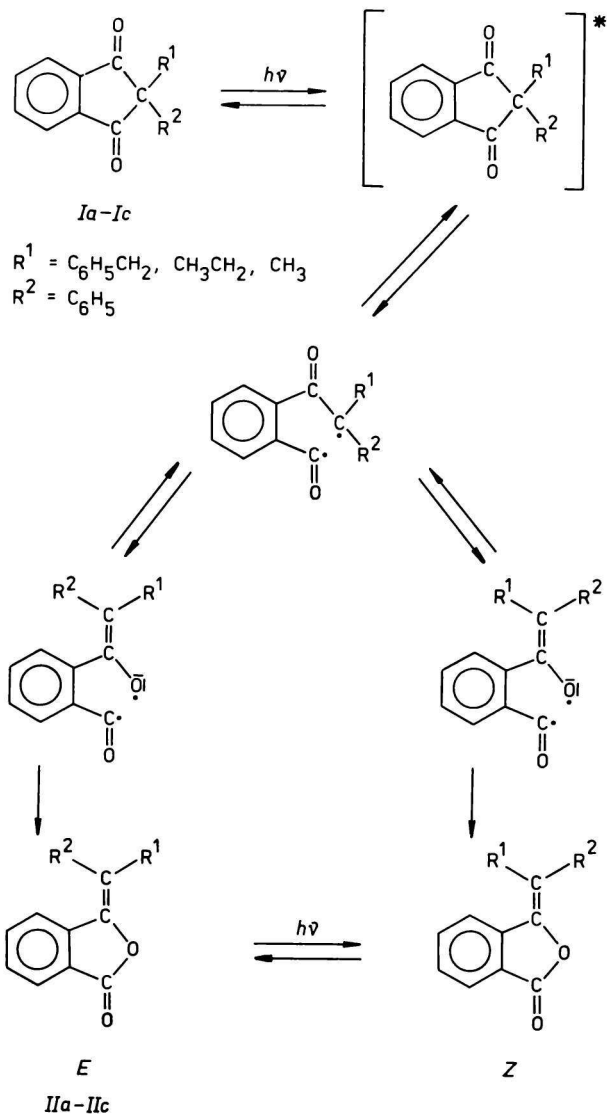
При фотохимической изомеризации 2-R-2-фенил-1,3-индандионов (R = C₆H₅CH₂, CH₃CH₂, CH₃) в соответствующие *E*,*Z*-дизамещенные метиленфталиды было обнаружено, что природа R влияет на соотношение *E*,*Z*-изомеров фталидов и *n*₂ выход изомеризации, но не влияет существенно на квантовый вывод. Обратная изомеризация образующихся фталидов в соответствующие 1,3-индандиона не наблюдалась.

The French authors *Rigaudy* and *Derible* [1, 2] indicated possibility of photochemical isomerization of 2-mono- and 2,2-disubstituted 1,3-indanediones to a mixture of substituted *E*- and *Z*-methylenephthalides and *vice versa*, e.g. photoisomerization of phthalides to the corresponding derivatives of 1,3-indanedione.

The above-mentioned photoisomerization can be interpreted either by a photolytic cleavage of the C-1—C-2 bond in the indanedione skeleton (Norrish Type I Process) or by a rupture of the C—O bond in the phthalide moiety (Scheme 1). The Norrish cleavage is most often accounted for the photoisomerization of β -diketones to unsaturated lactones [3].

We have already studied photoisomerization of 2-phenyl-1,3-indanedione and found out that this compound undergoes photochemical conversion to *E*,*Z*-ben-

zylidenphthalide. However, contrary to the French authors' result, both *E*- and *Z*-benzalphthalides survived photochemical isomerization to the 2-phenyl-1,3-indanedione in our hands. Irradiation in this case led to a photostationary state of *E,Z*-benzalphthalide [4]. Such a finding prompted us to investigate behaviour of 2,2-disubstituted derivatives of 1,3-indanedione under the same conditions.



Scheme 1

Table 1

Spectral data of 2-R-2-phenyl-1,3-indanediones (*Ia—Ic*) and 3-(R-phenylmethylene)phthalides (*IIa—IIc*)

| Compound | R | UV | | IR $\bar{\nu}/\text{cm}^{-1}$ | | $^1\text{H NMR } \delta/\text{ppm}$ | | |
|------------|---------------------------------------------------------|------------------------------------------|---------------------------------------------------------------------|-------------------------------|-------------------|-------------------------------------|-----------------|-----------------|
| | | $\frac{\lambda_{\text{max}}}{\text{nm}}$ | $\log(\epsilon(\lambda_{\text{max}})/(\text{m}^2 \text{mol}^{-1}))$ | $\nu(\text{C=O})$ | $\nu(\text{C=C})$ | Ar | CH ₃ | CH ₂ |
| <i>Ia</i> | C ₆ H ₅ CH ₂ | 260 | 3.55 | 1720 | 1755 | 6.5—8.5 | | 3.6 |
| <i>Ib</i> | CH ₃ CH ₂ | 228 | 4.75 | 1695 | 1735 | 6.6—8.55 | 0.75 | 2.3 |
| <i>Ic</i> | CH ₃ | 227 | 4.85 | 1725 | 1765 | 6.5—8.65 | 1.65 | |
| <i>IIa</i> | <i>E</i> -C ₆ H ₅ CH ₂ | 315 | 3.93 | 1770 | 1695 | 6.4—9.1 | | 4.05 |
| <i>IIa</i> | <i>Z</i> -C ₆ H ₅ CH ₂ | 325 | 4.06 | 1780 | 1670 | 7.1—8.1 | | 4.30 |
| <i>IIb</i> | <i>E</i> -C ₂ H ₅ | | | | | 6.4—9.1 | 1.05 | 2.78 |
| <i>IIb</i> | <i>Z</i> -C ₂ H ₅ | | | | | 6.9—8.5 | 1.19 | 2.93 |
| <i>IIc</i> | <i>E</i> -CH ₃ | | | | | 6.6—8.6 | 2.35 | |
| <i>IIc</i> | <i>Z</i> -CH ₃ | | | | | 6.8—8.7 | 2.53 | |

Experimental

The studied 2-R-2-phenyl-1,3-indanediones *I* (R = CH₃, C₂H₅, CH₂-C₆H₅) were prepared by alkylation of 2-phenyl-1,3-indanedione salt with corresponding alkyl halides [5, 6]. The crude products were purified by crystallization from benzene. Their spectral data are presented in Table 1.

Preparative photochemical isomerization was carried out in a photochemical reactor with a quartz finger. The light of 125 W mercury discharge lamp RVK was filtered through simax glass. The course of photochemical reactions was monitored by UV spectra taken on a UV VIS, RIR PE 50 spectrometer. IR spectra were recorded on a PE 180 spectrometer and ¹H NMR spectra were measured on a Tesla BS 487 instrument with 80 MHz working frequency.

The quantum yields were measured in an apparatus consisting of a high-pressure mercury discharge lamp Osram HBO 200 or medium-pressure discharge lamp RVI 125 working in medium-pressure or low-pressure discharge of the monochromator M 300 with output of light-beam in the UV region (Applied Photophysics), tempering block, beam divider, photoelectric cells, integrator, and magnetic stirrer (scheme presented in [4]).

The studied compounds were irradiated in a 1 cm × 1 cm quartz cell. By means of a calibration curve (potassium ferric oxalate) for the given wavelength we determined the light intensity impinging on the cell containing the reaction mixture. The samples were degassed three times at 0.014 Pa.

Photoisomerization of 2-R-2-phenyl-1,3-indanedione (*I*)

A solution of 2-R-2-phenyl-1,3-indanedione (R = benzyl, ethyl, methyl; 0.2 mmol) in benzene, anal. grade (200 cm³) was irradiated in a photochemical reactor for 61/2 h. The reaction course was monitored by electronic spectra. After the reaction was complete, the solvent was removed and the residue chromatographed on silica gel (L 100/125) using cyclohexane—benzene (volume ratio = 1 : 9) mixture as eluant. The starting compound was eluted first, followed by *Z*- and then by *E*-isomer. The yields and characteristics of the compounds are presented in Tables 1 and 2.

Table 2

Results of photoisomerization of 2-R-2-phenyl-1,3-indanediones in benzene at $\lambda_{exc} = 366$ nm

| R | Yield of phthalide/% | | | Quantum yield Φ | c/(mol/dm ³) |
|-----------------------------------------------|----------------------|----------|----------|-------------------------|--------------------------|
| | Total | Z-isomer | E-isomer | | |
| C ₆ H ₅ CH ₂ | 92.1 | 61.5 | 30.6 | 0.073 | 10 ⁻⁴ |
| CH ₃ CH ₂ | 28.1 | 18.7 | 9.4 | 0.076 | 10 ⁻⁴ |
| CH ₃ | 18.0 | 9 | 9 | 0.80 | 10 ⁻⁴ |

Results and discussion

The presence of $n\pi^*$ and $\pi\pi^*$ chromophores in molecules of 2-phenyl-1,3-indandione and 3-benzylidenephthalide derivatives determines their photochemical behaviour. The energy of orbitals, corresponding to individual transitions, is dependent on the structure; e.g. on the substitution in the original 2-phenyl-1,3-indandione. The absorption spectra of the studied 2-R-2-phenyl-1,3-indandiones ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$) exhibit in the UV region a weak absorption band at about $\lambda = 380$ nm and intensive one at about $\lambda = 260$ nm. The molar absorption coefficient of the former band is low for all derivatives and its position is only slightly altered by a polarity of the solvent and by the nature of R. Therefore, in agreement with the literature [4], the $S_1(n\pi^*)$ nature can be assigned to this band. The second intensive band at 260 nm is clearly distinguished from the previous one. The energy of this transition is sensitive to the solvent polarity, i.e. the absorption maximum is shifted to higher wavelengths in more polar solvents. This band bears the characteristics of the $S_1(\pi\pi^*)$ nature. All those facts determined the photochemical behaviour of the investigated indandiones.

Photolysis of the starting 2-R-2- C_6H_5 -1,3-indandiones ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$) by monochromatic light ($\lambda_{\text{exc}} = 366$ nm) brings about the Norrish α -cleavage. The preliminarily formed biradical affords the corresponding *E*- and *Z*-isomers of phthalides (Scheme 1). Conversion of the reaction is strongly dependent on R (Table 2) and ranges from 18 % ($R = \text{CH}_3$) to 92 % ($R = \text{C}_6\text{H}_5\text{CH}_2$). Such a dependence is probably due to stability of the biradicals (Scheme 1). Quantum yields are relatively low though somewhat higher than in case of photoisomerization of 2-phenyl-1,3-indandione [4] and practically unaffected by the substituent. The proportion of *E*- and *Z*-isomers of phthalides at a photostationary state was determined by means of ^1H NMR spectra. In case of 3-(benzylphenylmethylene)phthalide, both *E*- and *Z*-isomers were also isolated as individual compounds by preparative chromatography on silica gel (see Experimental). It can be seen from the data given in Table 2 that mutual proportion of *E*- and *Z*-isomers of phthalides is influenced by the substituent R, most probably by its steric demands. The time dependence of the degree of photoisomerization of the investigated indandiones was found not to be linear (Fig. 1). However, such a dependence is linear in case of those 1,3-indandione derivatives which on photoisomerization give exclusively one stereoisomer of phthalide [7]. For that reason we assume that photoisomerization of indandiones to phthalides is followed by formation of a photostationary state of the *E*- and *Z*-isomers of phthalides.

An attempt to perform photoisomerization of (*E,Z*)-3-(benzylphenylmethylene)phthalide (*Ila*) to the corresponding 1,3-indandione derivative was unsuccessful. This is in accord with our previous work [4] but in contradiction with the findings of the French authors [1, 2]. The result supports our explanation of the

failure to isomerize benzylidenephthalide to 2-phenyl-1,3-indandione. The lowest excited state of the investigated 1,3-indandione derivatives is that of the $T_1(n\pi^*)$ nature. Vacancies in the n -orbital of this excited state permit the Norrish cleavage I which is then followed by isomerization of preliminarily formed biradical (Scheme 1). In the case of phthalides *Ila*—*Ilc*, similarly as in the case of benzylidenephthalide, the $S_1(n\pi^*)$ absorption band is completely overlapped by the intensive $S_1(\pi\pi^*)$ band. The lowest excited state has the $T_1(\pi\pi^*)$ nature and hence, this state cannot make α -cleavage possible. *E*—*Z* isomerization of substituted methylenephthalides takes place instead.

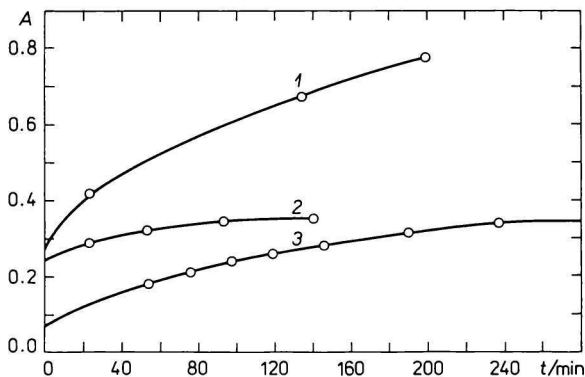


Fig. 1. Decrease of the amount of the starting compound in dependence on the reaction time.

1. 2-Benzyl-2-phenyl-1,3-indandione;
2. 2-methyl-2-phenyl-1,3-indandione;
3. 2-ethyl-2-phenyl-1,3-indandione.

References

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