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Stereochemistry in Control of Photochemical Reactivity: 2,6-diaryl-4*H*-spiro[cyclohexane-1,2'-indene]-1',3',4-triones

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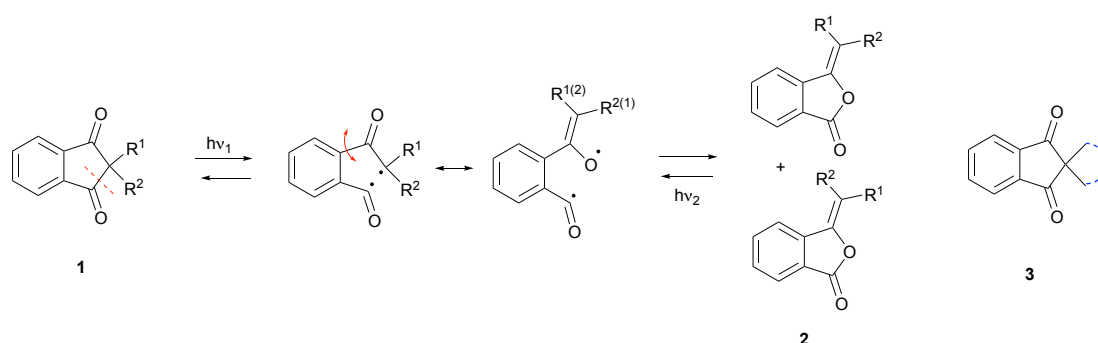
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Abstract. Photochemical reaction of *trans*-2,6-diaryl-4*H*-spiro[cyclohexane-1,2'-indene]-1',3',4-triones gives rise to the formation of the ylidenephthalide derivatives as previously observed for 2,2-disubstituted 1,3-indandiones. In contrast, the respective *cis*-isomers afford different products originating from the unprecedented reversible cyclohexanone cycle breaking (photo-induced retro-Michael reaction). The difference between the reaction pathways does not depend on the irradiation wavelengths or the light source power and is observed both in solution and solid state.

Keywords: 1,3-indandione, spiro-1,3-diketone, photochemistry, photochromism, photoacids

1. Introduction

Photochemical rearrangement of 2-mono and disubstituted 1,3-indandiones **1** into ylidenephthalides **2** (Scheme 1) is known since 1965.¹ A mixture of isomers is formed when R¹ and R² are different. This reaction is reversible and irradiation leads to a photostationary state, although the equilibrium is almost completely shifted toward the phthalides when one or both substituents are aryl groups.² Later it was demonstrated that 2-alkyl-2-acyl,³ 2-aryl-2-alkoxy⁴ and 2-aryl-2-amino⁵ derivatives of 1,3-indandione undergo the same rearrangement.



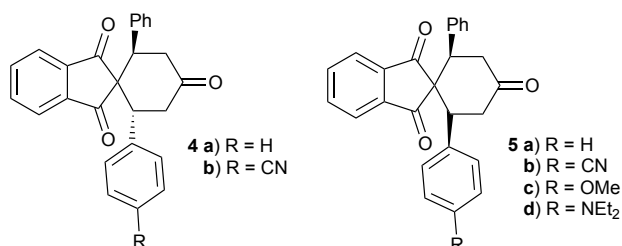
Scheme 1. Reversible photochemical conversion of 2-mono- and disubstituted 1,3-indandiones.

The generally accepted mechanism of this reaction is based on the Norrish type I pathway involving the primary photo-induced homolytic breaking of the C1-C2 bond and the following isomerization and re-cyclization.^{1a,2a,6} Analogous rearrangement between 2,2-dialkyl-1,3-indandiones and ylidenephthalides within the

respective cation radicals formed under electron ionization in a mass spectrometer prior to fragmentation was also reported.⁷

Derivatives **3** belonging to the same type of 2,2-disubstituted 1,3-indandiones are the focus of considerable synthetic efforts: over 30 research papers describing more than 400 new compounds of type **3** have been published only during the past five years.⁸ The interest toward derivatives **3** is motivated by the presence of the spiro-1,3-indandione moieties in various biologically active compounds, both natural⁹ and synthetic.¹⁰ Currently, development of new catalytic approaches allows the preparation of these derivatives stereo- and enantio-selectively from available precursors in 1 – 2 synthetic steps. However, the photochemical behavior of **3** has never been investigated, to the best of our knowledge, although these derivatives should be photoactive as well.

In the present paper, we report on the results of our investigation on the photochemical behavior of substituted 2,6-diphenyl-4*H*-spiro[cyclohexane-1,2'-indene]-1',3',4-triones, which can be isolated as the *trans*- (**4**) and *cis*- (**5**) isomers.¹¹



These derivatives, except **5d**, are known and recognized as the most promising from the point of view of biological activity.^{10b} In spite of the recent progress,^{8i,j,n} it is often difficult to prepare the *trans*-isomers without admixture of more thermodynamically stable *cis*-isomers, and we limited our study by **4a** and **4b** that can be isolated sufficiently pure.

2. Results

2.1. Photochemistry of *trans*-isomers (**4**)

The absorption spectra of **4a** and **4b** are practically identical. A broad weak (ϵ about 70) absorption band between 315 and 410 nm typical of $n \rightarrow \pi^*$ transitions and moderate intensity bands between 250 and 310 nm (ϵ between 1800 and 500) are present (Fig. 1). In spite of weak absorption, irradiation of derivatives **4** in

cyclohexane at 254 nm and in dichloroethane or ethyl acetate at 312 nm gives rise to a reaction; the typical changes in the absorption spectra are shown in Fig. 1 (Fig. S1 for **4b**). The same photoreaction is observed at 405 nm, however, several hours of irradiation needed to accumulate a noticeable amount of the product. The rate of the reaction at 312 nm, the maximum of absorption (320 nm) and the absorption band shape of the emerging product are similar to those described earlier¹ for the photo-rearrangement of 2-disubstituted 1,3-indandiones into the respective ylidenephthalide derivatives of type **2**. In preparative experiments, irradiation of a 1.5 mM solution of **4a** in ethyl acetate at 312 nm afforded a single, according to the NMR spectrum, product **6** (Scheme 2), the structure of which was finally confirmed by the X-Ray structure determination (Fig. 2). It is worth of noting that the *trans*-configuration of the phenyl groups is retained. The same reaction was observed upon irradiation of solid samples.

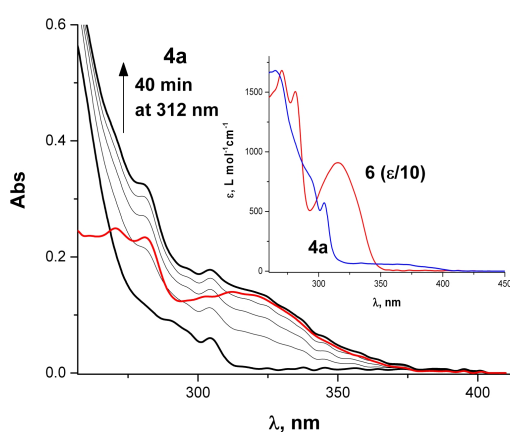
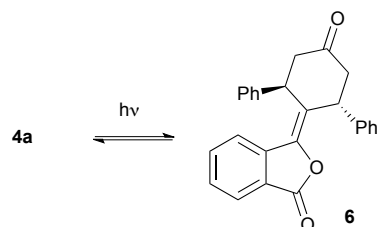


Fig. 1. Irradiation of **4a** in EtOAc during 40 min at 312 nm. Red: the difference between the final and initial spectra. Inset: blue – **4a** in ϵ , red – **6** in $\epsilon/10$.



Scheme 2. Reversible photochemical conversion of **4a** at 254, 312 and 405 nm.

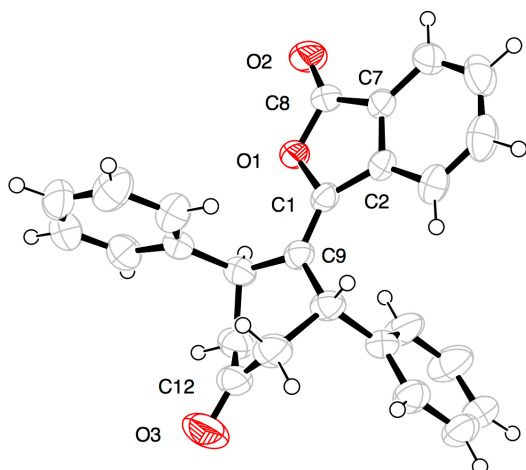


Fig. 2. ORTEP diagram (50% probability ellipsoids) of **6**. Selected bond lengths (Å). C1-O1: 1.408(2); O1-C8: 1.379(2); C8-O2: 1.196(2); C1-C9: 1.331(2); C12-O3: 1.210(3).

The yield of **6** after 4 h of irradiation was about 20% owing to the photo-reversibility of the reaction and strong absorption of **6** at 312 nm leading to a photostationary state. The photo-reversibility of this reaction has been confirmed by an independent experiment using an isolated pure sample of **6**. No preparative experiments were carried out on **4b**, but the absorption spectra changes during irradiation were practically the same as observed with **4a**.

2.2. Photochemistry of *cis*-isomers (**5**)

The absorption spectra of isomers **5** (Fig. 3) are very similar to those of **4**, although our preliminary calculations at the TD DFT level show that a weak absorption between 350 and 410 nm originates from different electronic transitions than the respective band of isomers **4**. Irradiation of the *cis*-isomer (**5a**) also gives rise to a photochemical reaction that, in this case, proceeds considerably faster than for the *trans*-isomer (Fig. 3). The reaction takes just 80 seconds at 312 nm and about 30 min at 405 nm. The main product exhibits a maximum at about 280 nm and cannot, therefore, be an ylidenephthalide derivative of type **2**. In ethanol and acetonitrile at room temperature, this product is converting back to the starting **5a** within several days. No change in the spectra of the irradiated solution was observed in dry 1,2-dichloroethane and ethyl acetate during several weeks.

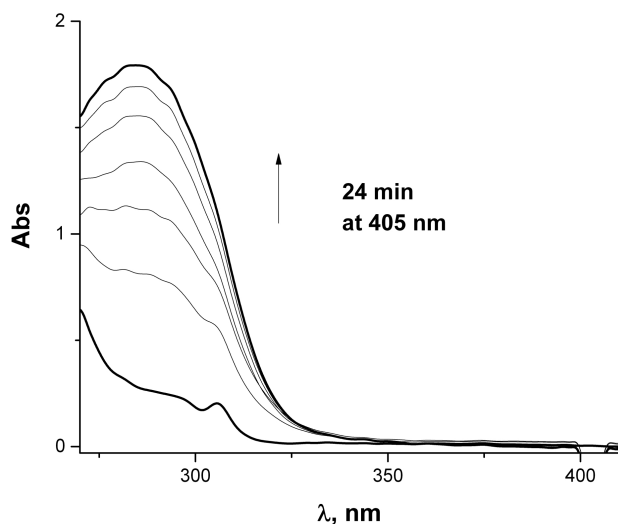


Fig. 3. Irradiation of **5a** in EtOAc during 24 min at 405 nm.

The same behavior was observed for derivatives **5b** and **c**. Thus, **5a – c** can be considered to behave as thermo-reversible photochromes with the outstanding stability of the photo-induced form.

Derivatives **5** do not react with DBU or weaker bases like triethylamine. The addition of a drop of DBU to the irradiated solution of **5a** led to the appearance of a broad absorption band centered at 440 nm characteristic of the 1,3-indandione anion.¹² Moreover, whereas **5a** does not quench fluorescence of *N*-isopropylcarbazole (NIPC), effective quenching was observed upon irradiation of **5a** in the presence of this acid-sensitive indicator¹³ (Fig. 4), evidencing thus the formation of an acidic product. The excitation wavelength was 350 nm, as absorption of the emerging product at this wavelength is negligible, at least at the initial stage of irradiation (Fig. 3). The experimental pK_a value of 2-methyl-1,3-indandione in water is known to amount 6.15 (the diketo form) and 4.19 (the enol form).¹⁴ The enol form of this derivative can be a stronger acid than acetic and benzoic acids also in non-aqueous solvents. No fluorescence quenching was observed using derivative **4a** under the same conditions.

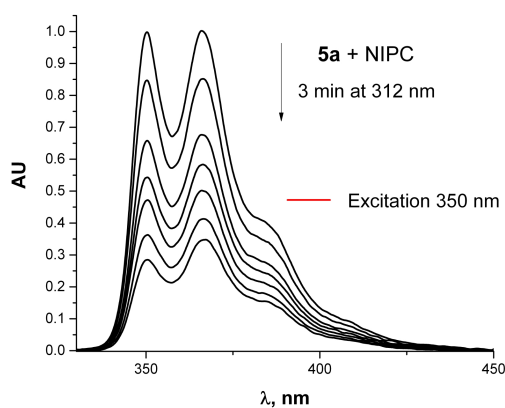


Fig. 4. Irradiation of a mixture of **5a** and NIPC (1.2×10^{-4} M) at 312 nm in ethyl acetate. Fluorescence was recorded every 30 s of irradiation.

The above observations suggested that the photoreaction involves breaking of a C-C bond within the cyclohexanone moiety and the formation of the mono-substituted 1,3-indandione derivative (a photo-induced retro-Michael reaction).

The preparative experiments were done at 312 and 405 nm, under the same conditions as for **4a**. At 312 nm, the degree of conversion reached 70% after 3 h of irradiation. The major part of the isolated solid (about 90%) consisted of a mixture of **7E** and **7Z** isomers (Scheme 3) along with 10% of **4a**, according to the ^1H NMR spectra (Fig. 5a). The chemical shifts of protons H_a , H_b , H_c and H_d and their splitting patterns are similar to those observed for derivatives of the type $(\text{RCO})_2\text{CH-CHPh-CH}_2\text{-CO-R}_1$.¹⁵ Interestingly, the formation of isomer **7E** upon dissolution of **4a** or **5a** in methanol in the presence of sodium methanolate and subsequent acidification has been suggested previously basing on the analysis of the IR spectra of the crude precipitate.¹⁶ We reproduced this experiment and the NMR spectrum confirmed that it is indeed a mixture of **7E**, **4a** and **5a** (Fig. 5b). The presence of the *Z* isomer in our photochemical experiments may be explained by partial photo-isomerization of the *E* isomer.

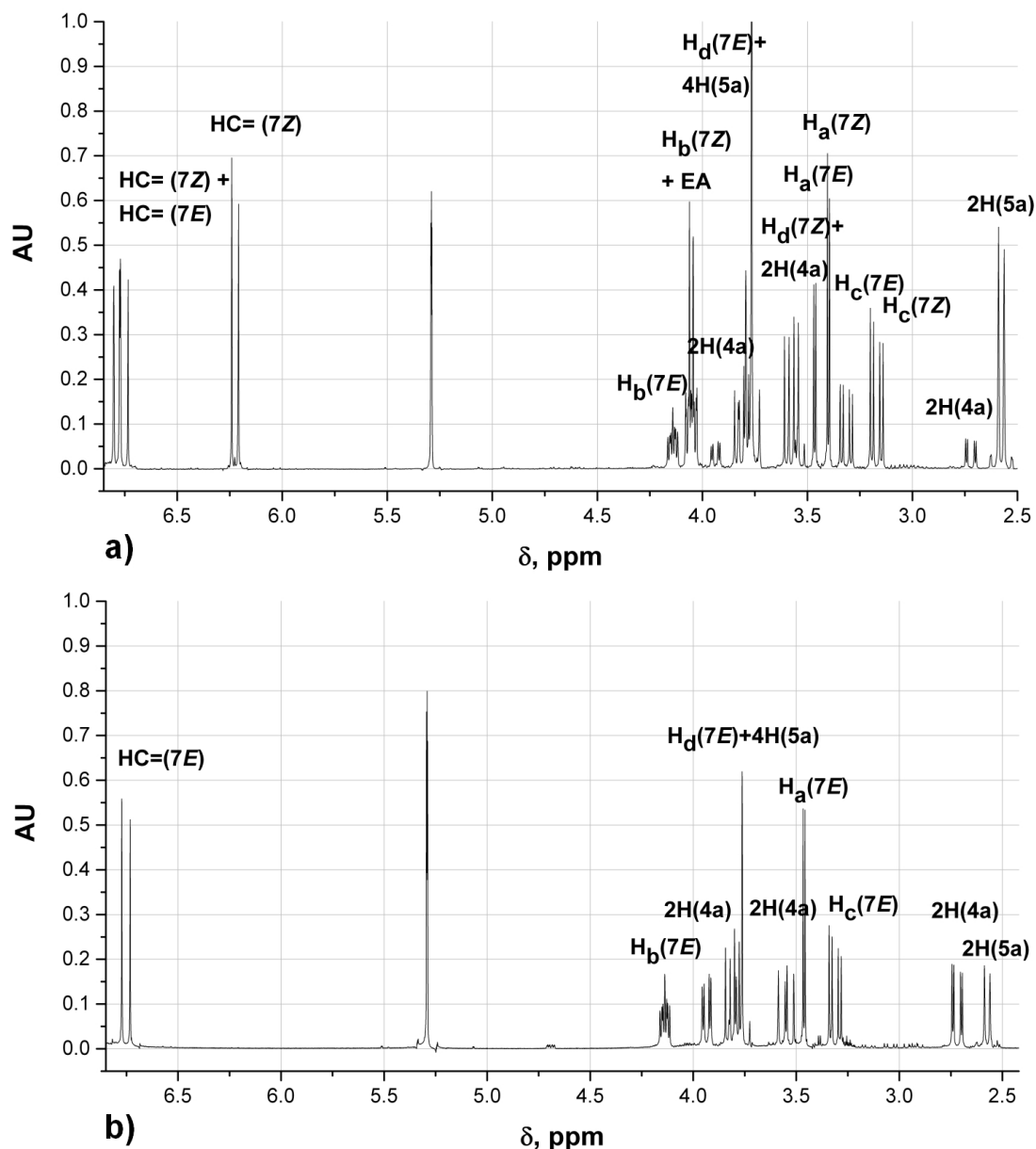


Fig. 5. a) ^1H -NMR spectrum of the isolated product mixture from the reaction of **5a** at 312 nm in ethyl acetate (EA). b) ^1H -NMR spectrum of the isolated product mixture from the reaction of **5a** with NaOMe in methanol and subsequent acidification according to¹⁶.

Upon irradiation at 405 nm, the degree of conversion was about 75% after 1.5 h of irradiation and the ^1H NMR spectrum indicated the presence of about 40% of **7** (*E* and *Z* isomers), 10% of **4a** and 25% of another compound, only traces of which were observed in the reaction mixture obtained at 312 nm. This compound, isolated by chromatography, is also photo-active and converts into the mixture of **7** (*E* and *Z* isomers), rapidly at 312 nm and slowly at 405 nm (Fig. 6). The structure of this compound as **8** (Scheme 3) was suggested by its NMR spectra and was confirmed by the X-Ray structure determination (Fig. 7).

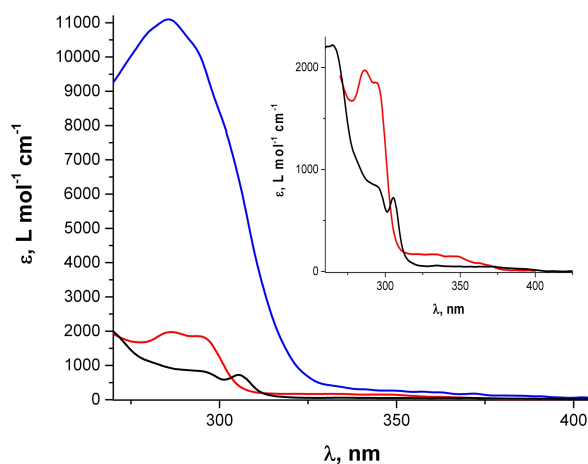


Fig. 6. Absorption spectra of **5a** (black), **8** (red) and **7** (blue, by irradiation of **8** at 312 nm). Inset: the rescaled spectra of **5a** and **8** revealing weak absorption between 315 and 410 nm

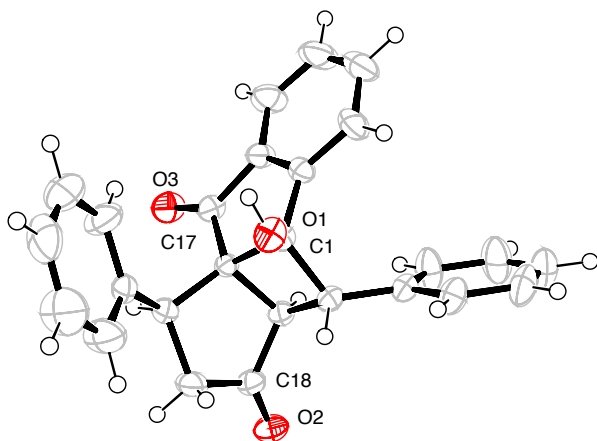
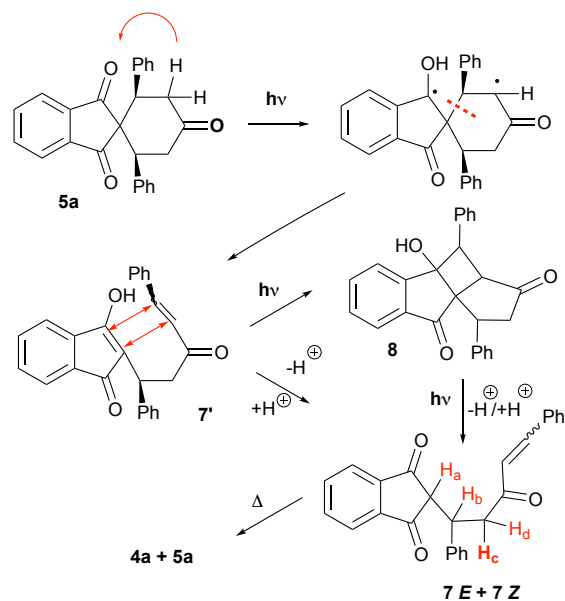


Fig. 7. ORTEP diagram (50% probability ellipsoids) of **8**. Selected bond lengths (Å). C1-O1: 1.401(3); C18-O2: 1.210(4); C17-O3: 1.221(4).

Our attempts to isolate pure **7 E** and **7 Z** isomers were unsuccessful, since these compounds easily convert into the cyclic isomers **5a** and **4a** upon contact with SiO₂, Al₂O₃ or heating, excluding the possibility of chromatographic separation or crystallization. Although **5a** forms **7 E/Z** upon irradiation and the latter reverts back to **5a** thermally, the formation of **4a** (about 7 – 10%) makes the photochromism not fully reversible.



Scheme 3. A tentative mechanism of photo- and thermal reactions occurring upon irradiation of **5a**.

The above observations allow suggesting a tentative mechanism for the reaction sequence (Scheme 3). Thus, unlike derivatives **4** reacting with light by the Norrish I process, derivatives **5** may follow the Norrish II pathway: initial hydrogen transfer from the CH₂ group can lead to the enolic form **7'** via the intermediate biradical. Enol **7'** can react with light to form **8** and, in parallel, converts into the more stable diketo isomer **7**. The ratio between **7** and **8** detected finally in the mixture is dependent on the wavelength of light interacting with the reaction mixture. This interpretation is corroborated by the available X-Ray structures of other known *cis*- and *trans*- isomers **4** and **5**^{8i,j} showing the presence of the C=O...H hydrogen bonds between one of the carbonyl groups of the 1,3-indandione moiety and the hydrogen atoms of the CH₂ groups in the boat conformation of the cyclohexanon moiety. Indeed, the absorption spectra of solutions of solid samples of **4a** and **5a** irradiated at 405 nm showed the same features as irradiation of their solutions.

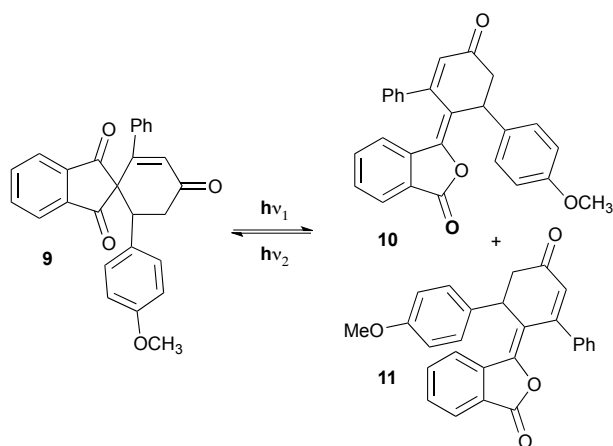
Our preliminary quantum mechanical calculations also confirm the presence of such intramolecular H-bonds (Fig. S2) within the thermodynamically more stable boat conformations. Therefore, both **4** and **5** could react according to the Norrish type II mechanism and the difference in their reactivity may be related to the different nature of the first lowest energy electronic transitions.

Upon irradiation, derivatives **5b** and **c** produced the same types of the products as **5a** (Figs S3, S4). However, owing to their asymmetrical structures, the number of

the photoproduct isomers increases and we limited ourselves by the analysis of the NMR spectra of the irradiated solutions.

Derivative **5d** is photochemically inert. Its absorption spectrum exhibits an extra broad longest wavelength band stretching between 330 and 450 nm (ϵ about 180 at 360 nm) and covering the weaker $n \rightarrow \pi^*$ bands. This band can be interpreted as a through-space charge transfer band from the electron donating *p*-dimethylaminophenyl moiety to the electron accepting 1,3-indandione moiety (Fig. S5).

To further investigate the influence of stereochemistry on the difference in photochemical reactivity, we prepared derivative **9**,¹⁷ in which the cyclohexane ring is more planar and the *trans* and *cis* isomers cannot exist. The structure of **9** has been confirmed by the X-Ray structure determination (Fig. S6).



Scheme 4. Reversible photochemical conversion of **4a** irradiated at 254 or 312 nm.

A relatively slow reaction, typical of the rearrangement into the phthalide derivatives, indeed, afforded two isomers **10** and **11** (Scheme 4, Fig. 8). Like in the case of derivatives **4a** and **b**, this reaction also occurs at 405 nm, but requires many hours of irradiation as well. The structure of **11** has been confirmed by the X-Ray structure determination (Fig. 9), derivative **10** cannot be separated free of the starting **9**, but the ¹H NMR spectra of the mixture confirms the structure unequivocally.

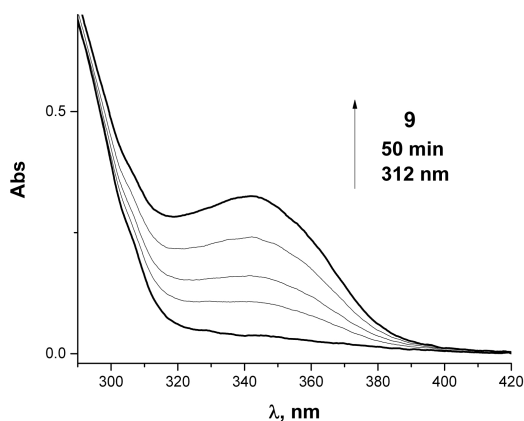


Fig. 8. Irradiation of **9** in EtOAc during 50 min at 312 nm.

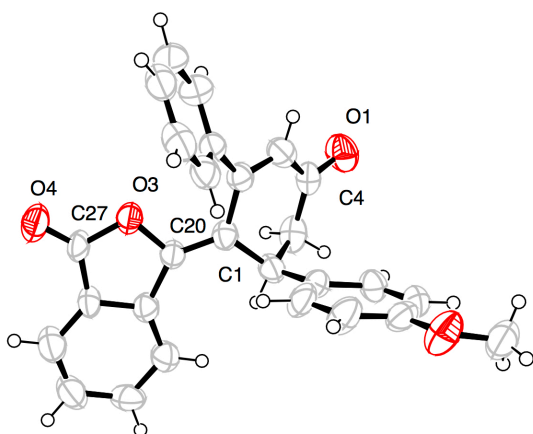


Fig. 9. ORTEP diagram (50% probability ellipsoids) of **11**. Selected bond lengths (Å). C4-O1: 1.255(8); C1-C20: 1.341(8); C20-O3: 1.411(7); C27-O3: 1.370(8); C27-O4: 1.207(8).

3. Conclusions

The photochemical reactions of 2,6-diphenyl-4*H*-spiro[cyclohexane-1,2'-indene]-1',3',4-triones are strikingly different for the *trans*- and *cis*-isomers **4** and **5**. We have identified the major products of these reactions and suggest a tentative mechanism for the photoreactions of **5**. The light sensitivity of these compounds, especially of isomers **5**, should be taken into account when bioactivity tests are carried out. Of particular interest is the formation of strongly acidic species from non-acidic precursors upon irradiation of **5**. Photo-isomerization of derivatives of type **4** and **9** might be a good alternative for preparation of bio-active ylidene-phthalides. We also find that the spiro-1,3-indandione derivatives involving 5-membered carbocycles and the analogs involving saturated cyclic 1,3-diketones (dimedone, Meldrum and

barbituric acids derivatives) are also photoactive. The photochemical reactions of these compounds are currently under investigation in our laboratory.

4. Experimental section

4.1. General methods

^1H and ^{13}C NMR spectra were recorded in methylene chloride- d_2 on JEOL ECS400 spectrometer at 399.78 and 100.53 MHz respectively. Proton chemical shifts are given in ppm downfield from tetramethylsilane and coupling constants (J) in Hertz.

The X-Ray crystallography data were collected on a Bruker-Nonius KappaCCD diffractometer with CCD detector using MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication: **6** CCDC 1578550, **8** CCDC 1578551, **9** CCDC 1578552, **11** CCDC 1578553.

The UV–Vis absorption were recorded with Ocean Optics USB 4000 and JASCO V-660 in 2, 4, 10 and 100 mm quartz cells. Irradiation of solutions for the UV-Vis control was done using a UVP LLC 95000505 lamp (254 nm), LED sources LUMOS 43 (Atlas Photonics) at 300, 315, 330, 350, 405 nm. For the preparative scale photochemical reactions, UV Transilluminator UST-2OM-8R (Biostep), 312 nm and CW laser Module Oxxius LBX-405-500-HPE-PP 405 nm at 200 mW (not focused beam) were used.

The starting spiro-1,3-indandiones were prepared according to the published procedures: **4a**,^{11a} **4b**,^{8ij} **5a-c**,^{11b} **9**.¹⁷ **5d** prepared analogously to^{11b}.

4.1.1. *2-[4-(dimethylamino)phenyl]-6-phenyl-4H-spiro[cyclohexane-1,2'-indene]-1',3',4-trione, cis-isomer (5d)*. Bright yellow crystals, yield 56%, m.p. 184-185°C. ^1H NMR: 7.63 (d, $J = 7.9$, 1H), 7.49-7.39 (m, 3H), 7.01-6.91 (m, 5H), 6.77 (d, $J = 8.9$, 2H), 6.25 (d, $J = 8.8$, 2H), 3.82-3.68 (m, 4H), 3.10 (q, $J = 7.0$, 4H), 2.55-2.49 (m, 2H), 0.91 (t, $J = 7.0$, 6H). ^{13}C NMR: 208.27 (CO), 203.82 (CO), 202.23 (CO), 147.04 (C), 143.24 (C), 143.00 (C), 138.03 (C), 135.07 (2CH), 129.84 (2CH), 128.17 (2CH), 127.41 (CH), 122.18 (CH), 111.43 (2CH), 62.52 (C), 48.58 (CH), 48.27 (CH), 44.10

(2CH₂), 44.00 (CH), 43.53 (CH), 12.10 (2CH₃). Calc.: C, 79.80; H, 6.47; N, 3.10. C₃₀H₂₉NO₃. Found: C, 79.94; H, 6.50; N, 3.04.

4.1.2. Irradiation of **4a** at 312 nm. 3-(4-oxo-2,6-diphenylcyclohexylidene)-2-benzofuran-1(3H)-one, *trans*-isomer (**6**). A solution of **4a** (300 mg) in 600 ml of dichloroethane was irradiated in a quartz beaker at 312 nm during 4 h. After evaporation, the colorless solid consisted of about 80% of **4a** and 20% of **6** according to the ¹H NMR spectrum. The mixture was washed with ethanol to separate the major part of poorly soluble **4a**, ethanol evaporated and the residue (150 mg) was chromatographed in a column (SiO₂, hexane:EtOAc 5:1). The fraction with R_f = 0.2 afforded, after crystallization from ethanol, 30 mg (10%) of **6**, m.p. 220-221°C, as colorless needles. ¹H NMR: 7.88 (dd, *J* = 6.5, 1.4, 1H), 7.55-7.46 (m, 2H), 7.40-7.18 (m, 11H), 5.07 (d, *J* = 4.6, 1H), 4.96 (dd, *J* = 4.8, 2.9, 1H), 2.93 (td, *J* = 16.2, 1.8, 2H), 2.82 (td, *J* = 19.8, 4.1 2H). ¹³C NMR: 207.91 (CO), 166.05 (CO), 145.52 (C), 141.98 (C), 141.29 (C), 136.96(C), 134.64 (CH), 129.76 (CH), 129.24 (2CH), 128.88 (2CH), 127.33 (2CH), 127.22 (CH), 127.14 (2CH), 126.79 (CH), 125.90 (C), 125.61 (CH), 123.82 (CH), 120.72 (CH), 45.03 (CH), 43.70 (CH), 39.92 5(CH₂), 39.49 (CH₂). Calc.: C, 82.08; H, 5.30. C₂₆H₂₀O₃. Found: C, 82.14; H, 5.21.

4.1.3. Irradiation of **5a** at 405 nm. 4a-hydroxy-1,4-diphenyl-4,4a-dihydro-1H-cyclopenta[2,3]cyclobuta[1,2-a]indene-3,9(2H,3aH)-dione (**8**). A solution of 200 mg of **5a** in 400 ml of EtOAc in an open flask was irradiated for 2 h from above by the laser unfocused beam (at 200 mV) under continuous stirring. After evaporation, the residue was chromatographed in a column (SiO₂, methylene chloride). The first fraction was a mixture of **7** (*Z*- and *E*-isomers), **4a** and **5a** (90 mg), according to the ¹H NMR spectrum. The second fraction (30 mg, R_f = 0.15) after evaporation and double crystallization from ethanol afforded 18 mg (9%) of **8** as colorless needles, m.p. 202 – 203°C. ¹H NMR: 7.86 (d, *J* = 7.7, 1H), 7.39 (td, *J* = 7.6, 1.0, 1H), 7.30 (td, *J* = 7.5, 1.2, 1H), 7.19 (d, *J* = 4.4, 3H), 7.07 (d, *J* = 1.7, 1H), 6.81 (d, *J* = 7.7, 1H), 6.71 (dd, *J* = 7.4, 2.1, 2H), 4.58 (dd, *J* = 14.3, 7.8, 1H), 4.01 (d, *J* = 6.3, 1H), 3.76 (dd, *J* = 16.9, 14.6, 1H), 2.94 (ddd, *J* = 16.9, 7.9, 1.7, 1H), 2.80 (d, *J* = 6.2, 1H). ¹³C NMR: 212.62 (CO), 203.00 (CO), 152.85 (C), 138.61 (C), 137.18 (C), 136.79 (C), 135.09 (CH), 129.71 (CH), 128.73 (2CH), 128.15 (2CH), 127.62 (2CH), 127.25(CH), 127.18 (2CH), 126.98 (CH), 126.09 (CH), 123.42 (CH), 83.56 (CHOH), 61.55 (CH), 49.46

(CH), 41.23 (CH), 41.01(CH₂). Calc.: C, 82.08; H, 5.30. C₂₆H₂₀O₃. Found: C, 81.94; H, 5.27.

4.1.4. Irradiation of 5a at 312 nm. Solutions of **5a** in EtOAc (concentration about 0.015 mmol/l) were irradiated in a quartz beaker for 3 h. After evaporation of the solvent, the oily residue was analyzed by ¹H NMR spectra (Fig. 5). The ratio of Z/E isomers of **7** varied to some extent in different runs.

4.1.5. Irradiation of 9 at 312 nm. (Z)-3-(4-methoxy-5'-oxo-5',6'-dihydro-[1,1':3',1''-terphenyl]-2'(1'H)-ylidene)isobenzofuran-1(3H)-one (11). A solution of 120 mg of **9** in cyclohexane was irradiated at 312 nm in a quartz beaker for 6 h. During this time, according to ¹H NMR spectrum, 80% of the starting compound was converted into two products. Column chromatography (SiO₂, cyclohexane:EtOAc 4:1) afforded a mixture of **9** and **10** as yellow oil. Further elution with a more polar mixture (3/1) gave the second fraction as yellow solid. The solid was washed with hot heptane and crystallized from ethanol. The yield of pure **11** was 30 mg (25%) as yellowish leaflets, m.p. 198 – 199°C. ¹H NMR (CDCl₃): 8.02 (d, *J* = 8.1, 1H), 7.95 (d, *J* = 7.6, 1H), 7.75 (t, *J* = 7.7, 1H), 7.63 (t, *J* = 7.5, 1H), 7.41-7.27 (m, 8H), 6.87 (d, *J* = 8.8, 1H), 6.15 (s, 1H), 5.16 (d, *J* = 3.6, 1H), 3.76 (s, 3H), 3.28 (d, *J* = 17.0, 1H), 3.07 (dd, *J* = 17.0, 5.5, 1H). ¹³C NMR (CDCl₃): 196.62 (CO), 164.93 (CO), 158.94 (CO), 154.88 (C), 145.63 (C), 139.59 (C), 138.04 (C), 135.06 (CH), 131.07 (CH), 130.96 (C), 129.62 (C), 129.60 (CH), 128.53 (2CH), 127.96 2CH), 127.22 (2CH), 126.46 (CH), 126.34 (C), 123.74 (CH), 120.58 (CH), 114.59 (2CH), 55.38 (CH₃), 42.83 (CH), 41.10 (CH₂). Calc.: C, 79.40; H, 4.94. C₂₇H₂₀O₄. Found: C, 80.15; H, 5.10.

¹H NMR of **10** (by subtraction of the spectrum of pure **9** from the spectrum of the mixture of **9** and **10**): 7.87 (d, *J* = 7.7, 1H), 7.44-7.24 (m, 6H), 7.28 (d, *J* = 8.7, 2H), 7.16 (t, *J* = 7.7, 1H), 6.81 (d, *J* = 8.7, 2H), 6.36 (s, 1H), 6.30 (d, *J* = 8.2, 1H), 5.36 (d, *J* = 4.4, 1H), 3.73 (s, 3H), 3.71 (d, *J* = 7.0 Hz, 1H), 3.20 (d, *J* = 17.7, 1H), 2.98 (dd, *J* = 17.7, 5.6 Hz, 1H).

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Supplementary data

Supplementary data related to this article including the absorption spectra of **4b**, **5b**, **5c**, **5d**, optimized geometry of **5a** and the ORTEP diagram of **9** can be found at:

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