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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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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.

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 R^1 and R^2 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-alkoxy[4] and 2-aryl-2-amino[5] derivatives of 1,3-indandione undergo the same rearrangement.

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 natural[9] 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]

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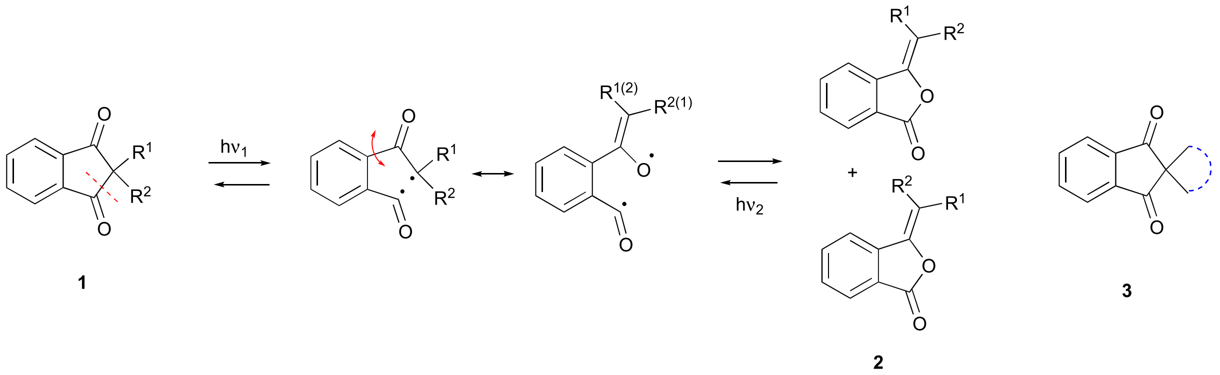
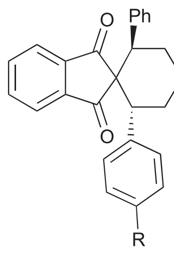
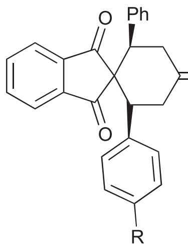


Scheme 1. Reversible photochemical conversion of 2-mono- and disubstituted 1,3-indandiones.



4 a) R = H
b) R = CN



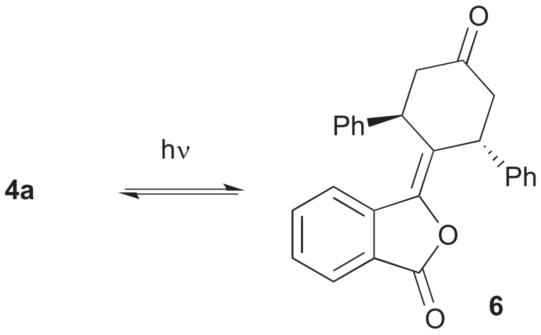
5 a) R = H
b) R = CN
c) R = OMe
d) R = NEt_2

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->π* 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



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

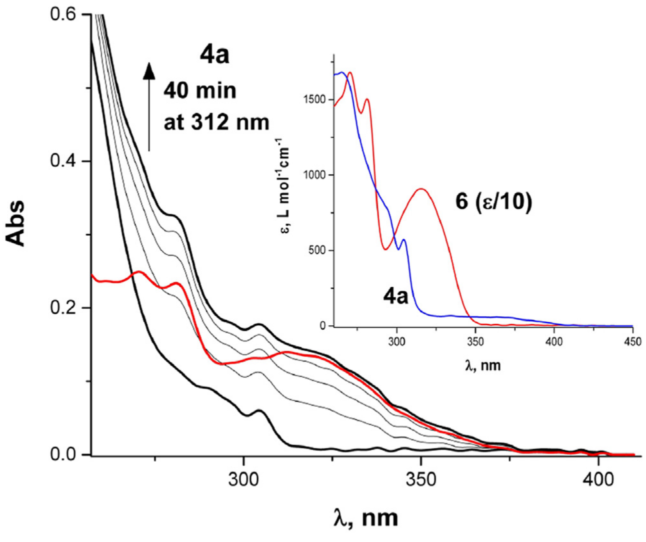


Fig. 1. Irradiation of **4a** in EtOAc during 40 min at 312 nm. Red: the difference between the final and initial spectra. Inset: blue – **4a** in ε, red – **6** in ε/10.

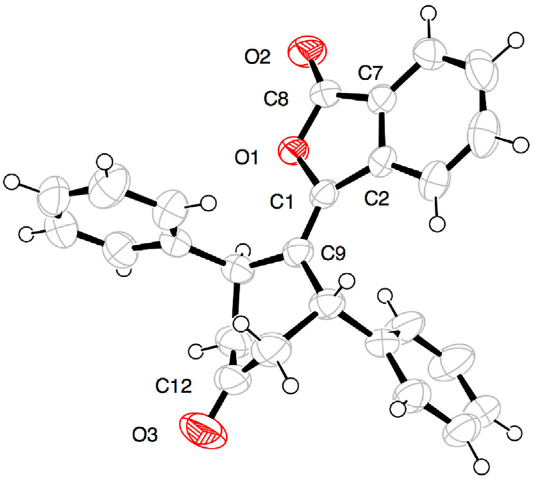


Fig. 2. ORTEP diagram (50% probability ellipsoids) of **6**. Selected bond lengths (Å). C1–O1: 1.408(2); O1–C8: 1.379(2); C8–O2: 1.196(2); C1–C9: 1.331(2); C12–O3: 1.210(3).