



# Spiro 1,3-indandiones: intramolecular photochemical reactions of carbonyl groups with carbon-carbon double bonds

Vladimir Lokshin, Hervé Clavier, Vladimir Khodorkovsky

## ► To cite this version:

Vladimir Lokshin, Hervé Clavier, Vladimir Khodorkovsky. Spiro 1,3-indandiones: intramolecular photochemical reactions of carbonyl groups with carbon-carbon double bonds. *New Journal of Chemistry*, 2020, 44, pp.14373-14378. 10.1039/D0NJ02923H . hal-02909637

**HAL Id: hal-02909637**

**<https://hal.science/hal-02909637>**

Submitted on 10 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Spiro 1,3-indandiones: intramolecular photochemical reactions of carbonyl groups with carbon–carbon double bonds†

Vladimir Lokshin,<sup>a</sup> Hervé Clavier<sup>b</sup> and Vladimir Khodorkovsky<sup>id</sup> \*<sup>a</sup>

2-Substituted 1,3-indandione derivatives are known to undergo a photochemical rearrangement into phthalides. We find that in the presence of a substituent involving a double carbon–carbon bond in the vicinity of the carbonyl group in spiro-1,3-indandiones, a variety of other types of intramolecular photochemical reactions readily occur: 1,3-acyl shift, intramolecular reversible Paternò–Büchi reaction, and formal oxa-[4+2]-cycloaddition. A specific feature of these reactions of spiro-1,3-indandiones is their photo-reversibility. The structures of polycyclic products of these reactions were determined spectroscopically and, in most cases, by single crystal X-ray structure determinations. A number of the products, especially those involving benzazulene or oxatricyclo[4.2.1.0<sup>3,8</sup>]nonane moieties are synthetic analogues of natural compounds of interest owing to a variety of their biological activities.

## Introduction

Intramolecular photochemical reactions of carbonyl groups with carbon–carbon double bonds such as oxa-di- $\pi$ -methane rearrangement,<sup>1</sup> 1,3-acyl shift<sup>2</sup> and intramolecular Paternò–Büchi reaction<sup>3</sup> have emerged as powerful synthetic methodologies. Among other photochemical methods,<sup>4</sup> these reactions are frequently used as key steps for the synthesis of complex polycyclic systems,<sup>5</sup> especially in the case of natural products and biologically relevant compounds.<sup>6</sup>

In spite of the large number of reports in this field and to the best of our knowledge, the use of the 1,3-indandione moiety as the carbonyl component in this type of photochemical reaction has been only scarcely investigated.<sup>7</sup> However, these intramolecular cycloaddition reactions could afford polycyclic systems involving the annelated indanone moiety. During the last decade, compounds of this type have attracted ever-growing attention, in particular, as potential precursors for the synthesis of biologically active derivatives.<sup>8</sup> Here, we report on the intramolecular photochemical reactions of 2-allyl- and spiro-1,3-indandione derivatives with the carbon–carbon double bonds constrained within the spiro-substituents, giving rise to a variety of products that are difficult to prepare using conventional non-photochemical approaches.

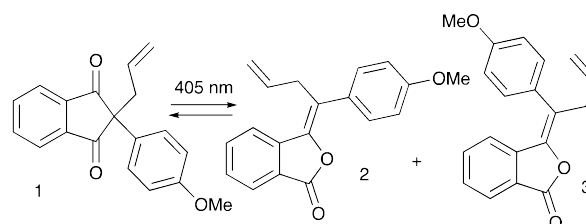
Spiro-1,3-indandiones by themselves attracted the interest of researchers owing to their versatile biological activity.<sup>9,10</sup>

## Results and discussion

### A reversible phthalide rearrangement

Initially, we assumed that 2,2-disubstituted 1,3-indandione **1** containing the allyl substituent will be a suitable substrate for the above-mentioned photoreactions. However, irradiation of this compound gave rise to the reversible phthalide rearrangement typical for 2-substituted 1,3-indandiones<sup>9</sup> (Scheme 1).

Unfortunately, owing to the low concentration of both photo-products in the photostationary state and similar polarities of isomers **2** and **3**, their separation by silica gel chromatography is complicated. We were able to successfully isolate pure isomer **2**, the structure of which was unambiguously confirmed by X-ray analysis of a single crystal (ESI,† Fig. S5). Therefore, we decided to investigate derivatives with more rigid structures involving carbon–carbon double bonds in the vicinity of the carbonyl groups, such as spiroindandiones **4–6** (Fig. 1).



Scheme 1 Photochemical reaction of 1,3-indandione 2-allyl derivative **1**.

<sup>a</sup> Aix Marseille Univ, CNRS, CINaM UMR 7325, Campus de Luminy – Case 913, 13288, Marseille, France. E-mail: khodor@cinam.univ-mrs.fr

<sup>b</sup> Aix Marseille Univ, CNRS, Centrale Marseille, iSm2, 13397 Marseille, France

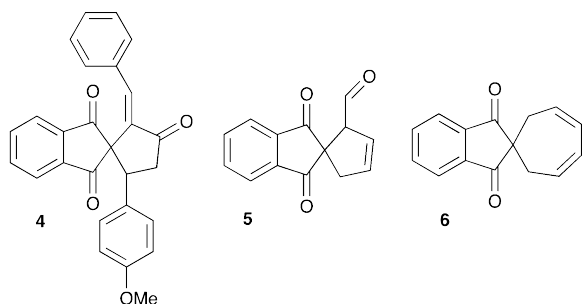


Fig. 1 Spiro-1,3-indandione precursors **4–6**.

#### Di- and tetrahydrobenzoazulenes from derivative **4**

Irradiation of **4** in various solvents (cyclohexane, dichloroethane and ethyl acetate) at 312 or 405 nm gives rise to considerable spectral changes (Fig. 2). The appearance of new absorption maxima at 300 nm evidences the formation of new products containing conjugated double bonds. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the mixture suggest that products possess a tricyclic structure involving a cycloheptenone fragment. In the preparative experiments, the highest conversion was achieved in ethyl acetate: only 5% of **4** remained unreacted and 80% of diastereomers **7** and **8** were detected by  $^1\text{H}$  NMR after four hours of irradiation (Scheme 2). The diastereomeric ratio, spanning from 2:1 to 1:2, was found to be a function of the irradiation time and the solvent polarity: the longer the irradiation time and the more polar the solvent, the greater the amount of **7** formed.

The above observations are consistent with Scheme 2 and are supported by the appearance of singlets at 5.4–5.5 ppm in the  $^1\text{H}$  NMR spectra corresponding to  $\text{H}_\alpha$  protons, disappearance of the signals at 200.1 and 201.1 ppm (carbonyls of the 1,3-indandione fragment) and the appearance of the signals at 186.3 and 188.3 (carbonyls of the cycloheptendione fragment) in the  $^{13}\text{C}$  NMR spectra.

The isolation of pure isomers **7** (*trans*) and **8** (*cis*) was found to be complicated since they are interconvertible, apparently *via* the enol form **9**. Chromatographic separation and crystallization

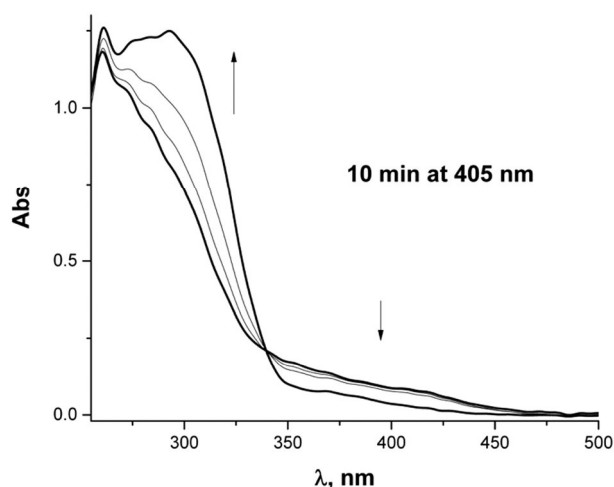
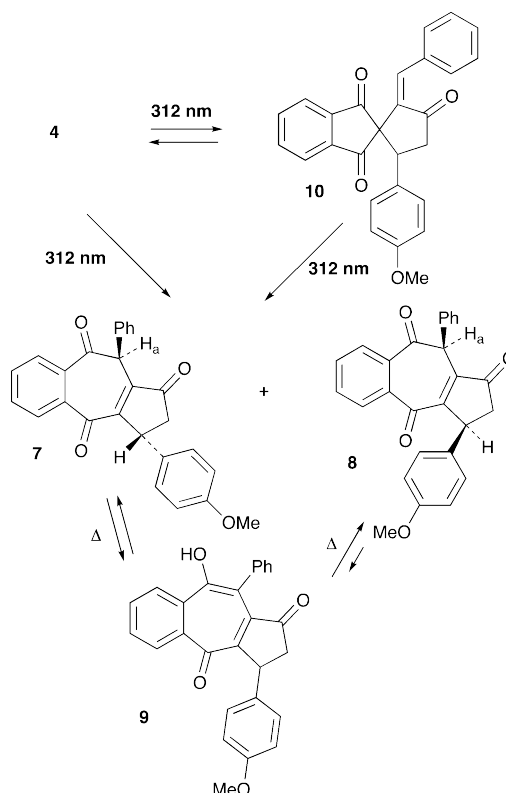


Fig. 2 Irradiation of derivative **4** in cyclohexane over 10 min.



Scheme 2 Photoreactions of derivative **4**.

from heptane afforded only the thermodynamically more stable diastereomer, which was identified as **7**. Compound **8** was not isolated in pure form. According to DFT calculations, **7** is more stable than **8** by 5.4 kcal mol $^{-1}$ . Its structure was unequivocally confirmed by single crystal X-ray structure determination (Fig. 3).

The formation of diastereomers **7** and **8** can in part also stem from the *E–Z* isomerization of the starting compound **4** occurring along the main photoreaction. The formation of *Z*-isomer **10** can be noticed at an early stage of the reaction by the appearance of the characteristic singlet signal of the =CH-Ph group at 6.25 ppm (7.85 ppm for **4**).

Rapid acidification of a crude mixture of isomers **7** and **8** in aqueous alkaline solutions afforded pure enol form **9**, since the

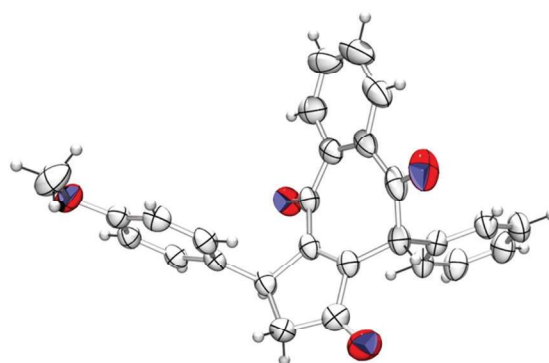
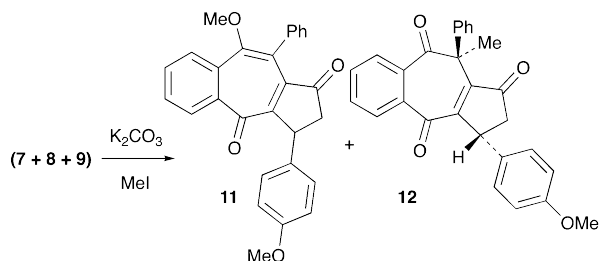


Fig. 3 ORTEP diagram (50% probability ellipsoids) of **7**.



Scheme 3 Synthesis of methylated derivatives **11** and **12**.

keto–enol equilibrium cannot be established in water owing to low solubility of **9**. This compound was found stable enough to be characterized spectroscopically, but during attempts of crystallization, **9** was converted back into a mixture of **7** and **8**.

When the crude photoreaction mixture was dissolved in water/ethanol solution of sodium hydroxide, slow acidification afforded a mixture of **7**, **8** and only a small amount of **9**. Methylation reaction of the crude mixture containing **7**, **8** and **9** with methyl iodide in acetone in the presence of potassium carbonate led to the formation of O- and C-methylated derivatives **11** and **12** (Scheme 3).

Both **11** and **12** were obtained as pure compounds by silica gel chromatography and their structures were confirmed by single crystal X-ray structure determinations (Fig. 4 and 5).

The most probable mechanism of the photoreaction of **4** involves an 1,3-acyl shift<sup>2</sup> including  $\alpha$ -cleavage and recyclization of the intermediate biradical, as shown in Scheme 4. Derivatives **7** and **8** are not photoactive and the equilibrium shifts toward the formation of tetrahydrobenzoazulene structures, although the relative stabilities of the isomer pairs **4** and **7**, **8** and **10** according to calculations are practically the same (within 0.1 kcal mol<sup>-1</sup>).

It should be mentioned that derivatives **7–9**, **11** and **12** involving the cycloheptendione and cycloheptenone fragments are the focus of numerous investigations related to their various biological activities. The great potential of 1,3-indandione derivatives as precursors for this type of compound has been highlighted in recent papers.<sup>11,12</sup> The presented photochemical approach supports this point of view.

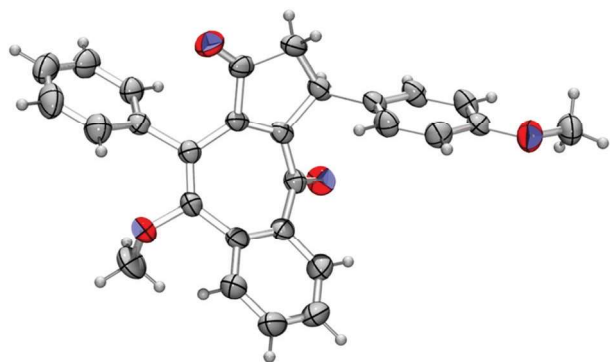


Fig. 4 ORTEP diagram (50% probability ellipsoids) of derivative **11**.

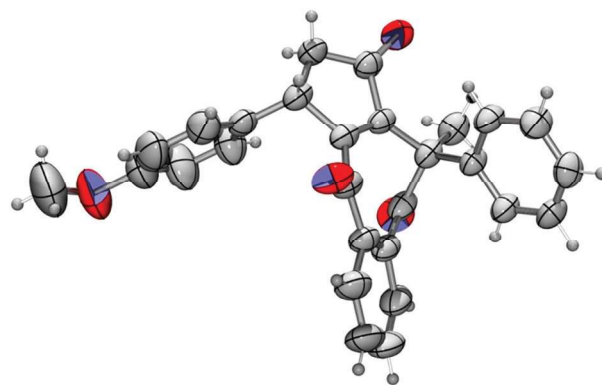
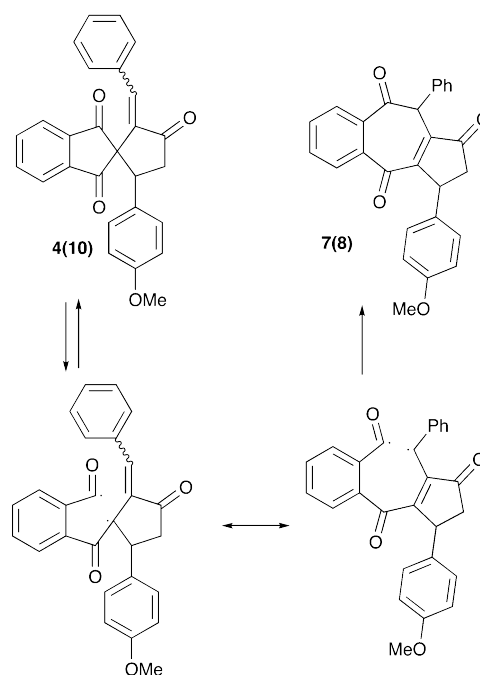


Fig. 5 ORTEP diagram (50% probability ellipsoids) of derivative **12**. One of two independent molecules is shown.



Scheme 4 Possible mechanism of the photoconversion of derivative **4**.

#### Reversible intramolecular Paternò–Büchi reaction of derivative **5**

Derivative **5** is also photoactive (Fig. 6). Irradiation of its solutions at 312 or 405 nm leads to a photostationary state with a low yield of a photo-product. Somewhat higher yields of this product, about 20% according to the NMR spectra, were observed by irradiation at 254 nm. Preparatively, the photo-product was isolated from the reaction at 254 nm in cyclohexane in 10% yield (30% on the reacted **5**) as a yellowish oil. Its structure as a polycyclic derivative **13** formed as a result of intramolecular Paternò–Büchi reaction (Scheme 5) was established by NMR spectroscopy. The fused (straight) oxetanes of type **13** can be distinguished from the bridged (cross) oxetanes of type **14** by the characteristic signal of the oxetane  $\alpha$ -protons, as noted previously.<sup>13,14</sup>

Derivative **13** can form four diastereomers in which the oxetane and cyclopentene fragments are in *syn*- and *anti*-configurations as

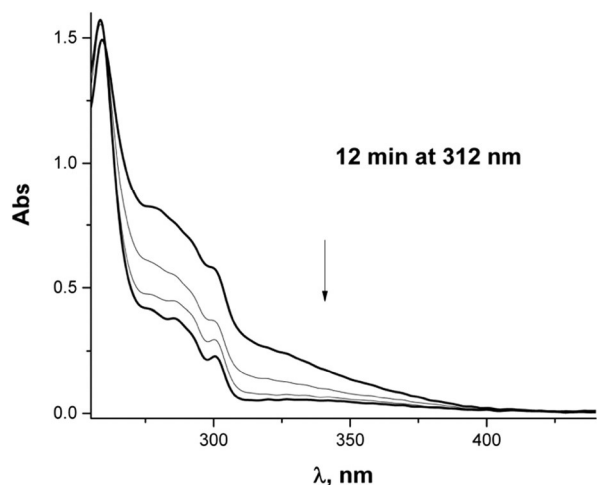


Fig. 6 Irradiation of derivative **5** in ethyl acetate over 12 min.

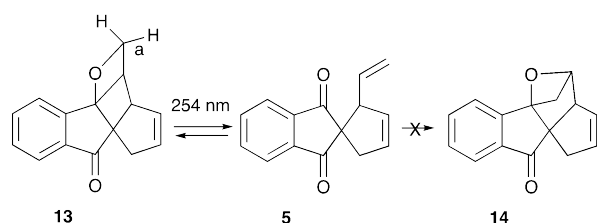
shown in Fig. 7 for the two most stable ones. DFT calculations also showed that the chemical shift of one of the  $\alpha$ -protons of the oxetane rings is the most sensitive to the configuration and the calculated  $^1\text{H-NMR}$  spectra indicate *syn*-configuration of **13** (Fig. S17 and S18 in ESI†). Moreover, the diastereomer in *syn*-configuration is more stable than *anti*-configuration by  $32.2 \text{ kcal mol}^{-1}$ .

The photo-reversibility of the reaction as depicted in Scheme 6 has been demonstrated in an independent experiment using a pure sample of **13**, irradiation of which in cyclohexane at 254 nm afforded the same photostationary state as irradiation of **5** (Fig. 8).

It is well known that oxetane cycles can afford alkenes and the carbonyl components pyrolytically,<sup>15</sup> catalytically,<sup>16</sup> under acidic conditions<sup>17</sup> and *via* electron transfer induced reaction.<sup>18</sup> To the best of our knowledge, there are no examples of photo-induced decomposition of the oxetane ring into initial components, in other words, the reversibility of the Paternò-Büchi reaction.

#### Oxatricyclononane derivative **15** from derivative **6**

Derivative **6** exhibits different photoreactivity. Irradiation of its solutions in ethyl acetate or cyclohexane at 312 nm gave rise to the rapid formation of a photostationary state containing, according to the UV-Vis and NMR spectra, about 75% of a product weakly absorbing at 312 nm (Fig. 9), which shifts the equilibrium toward the photoproduct. In a preparative experiment, the photo-product **15** was isolated as colorless crystals in 60% yield after the chromatographic separation and crystallization (Scheme 6). The structure of



Scheme 5 Photoreaction of derivative **5**.

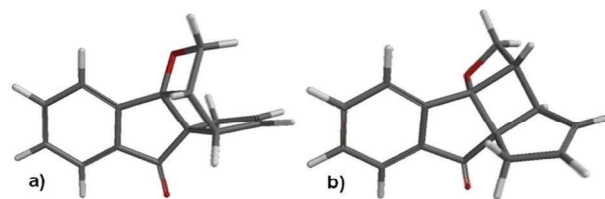
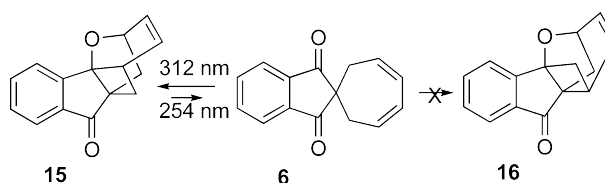


Fig. 7 Two diastereomers of **13**. (a) *syn*- and (b) *anti*-configuration.



Scheme 6 Photoreaction of derivative **6**.

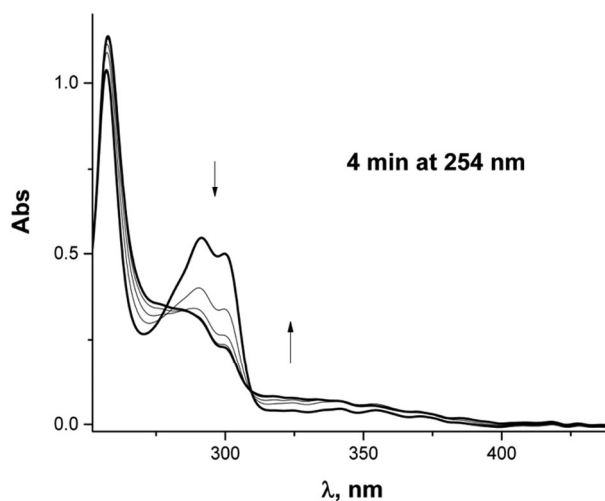


Fig. 8 Irradiation of derivative **13** in ethyl acetate over 4 min.

**15** was confirmed by the NMR spectra and the X-Ray structure determination (Fig. 10). The presence of another possible product **16**, which was calculated to be less stable than **15** by  $2.5 \text{ kcal mol}^{-1}$ , was not detected in the reaction mixture. Expectedly, derivative **15** partially converts into **6** upon irradiation of its solutions at 254 nm.

Derivative **15** involves a cage-like oxatricyclononane moiety very similar to the structure of the aglycone moieties of natural monoterpene glycosides (albiflorine, paeonivayin) isolated from *Paeonia* and possessing a wide range of biological activities.<sup>19</sup> Lactiflorine was for a long time believed to involve exactly the same oxatricyclo[4.2.1.0<sup>3,8</sup>]nonane backbone.<sup>20,21</sup> Only recently it was shown, thanks to total synthesis, that it possesses albeit a very similar but still a different structure of 2-oxatricyclo[4.2.1.0<sup>4,9</sup>]nonane.<sup>22,23</sup>

The oxatricyclic moiety involving the cyclobutane cycle is also an important part of marine natural bio-active products



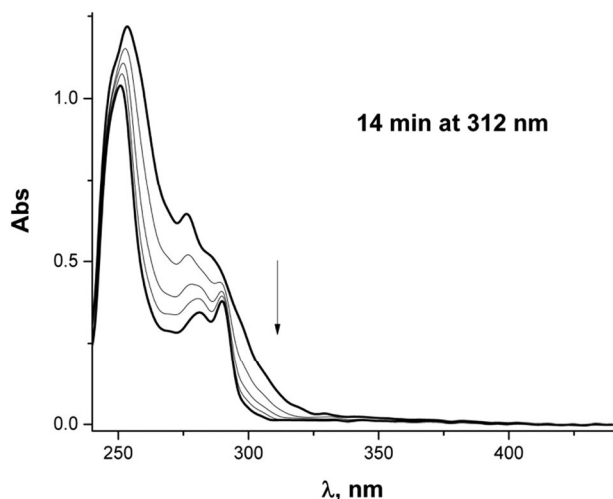


Fig. 9 Irradiation of derivative **6** in ethyl acetate over 14 min.

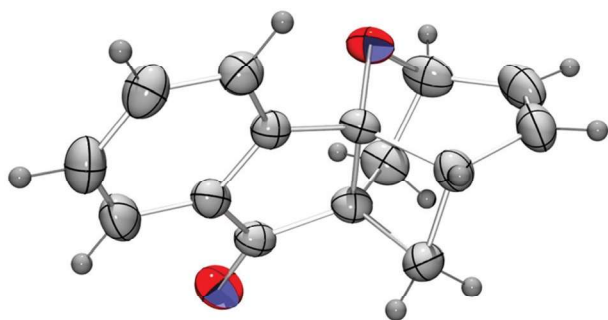
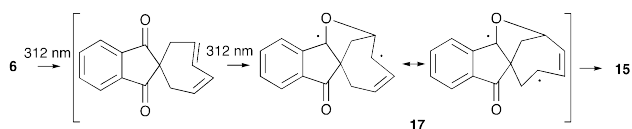


Fig. 10 ORTEP diagram (50% probability ellipsoids) of derivative **15**.

such as hippolachnin **A**,<sup>24</sup> bielschowskysin<sup>25</sup> and a series of cannabinoid.<sup>26</sup> All the above underscores the potential of **15** as a precursor for the synthesis of biologically active compounds.

A possible mechanism of the photo-reaction is not completely clear. Formally, the reaction involves an oxa-[4+2] cycloaddition of the carbonyl group and the diene group of cycloheptadiene. Similar photochemical reactions are known, although they are rare.<sup>27–29</sup> In our opinion, in this case, a pericyclic reaction is hardly possible. A more probable mechanism involves the isomerization of the *cis,cis*-cyclohexadiene moiety into the *cis,trans* isomer, the formation of biradical **17** and its subsequent cyclization as shown in Scheme 7. The formation of *cis,trans*-cyclohepta-1,3-diene as a transient intermediate in the photoreactions of the *cis,cis* isomer has been demonstrated.<sup>30</sup> In the case of derivative **6**, the follow up cyclization can be facilitated by the formation of C=O...H-CH= hydrogen bond.



Scheme 7 Possible mechanism of photoconversion of derivative **6**.

## Conclusions

We have demonstrated the diversity of the photochemical reactions within a series of spiro-1,3-indandiones. Thus, the carbonyl group of the 1,3-indandione moiety does not react with the double bond of the unconstrained allyl group (derivative **1**) and a well-known phthalide rearrangement occurred. In contrast, the double bonds in **5** and **6**, also separated from the 1,3-indandione moiety by one  $sp^3$  carbon atom, but partially restrained within the five- and seven-membered cycles, produce polycyclic products. Yet another reaction giving rise to the ring expansion of the indandione moiety into a seven-membered ring occurred in the case of derivative **4**, in which a double bond is directly connected to the indandione moiety. The light-induced conversions allowed the preparation of complex derivatives with potential biological activities in a limited number of steps. A certain limiting factor of using the photochemical step for synthesis purposes is often observed by the reversibility of the reaction stemming from the presence of the second carbonyl group. This drawback can be overcome by using the properly adjusted wavelength of irradiation. The scope and limitations of photochemical conversions of spiro-1,3-indandiones can be established after revealing the mechanistic details of the above reactions.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- (a) V. J. Rao and A. G. Griesbeck, Oxa-di- $\pi$ -methane rearrangement. in *Synthetic Organic Photochemistry*, ed. A. G. Griesbeck and J. Mattay, Marcel Decker, N.Y., 2005, ch. 7, p. 189; (b) V. J. Rao and K. Srinivas, Oxa-di- $\pi$ -methane rearrangement of  $\beta,\gamma$ -unsaturated ketones. in *CRS Handbook of Organic Photochemistry and Photobiology*, ed. A. Griesbeck, M. Oelgemöller and F. Ghetti, CRS Press, 3rd edn, 2012, ch. 22, p. 527.
- V. Singh, 1,3-Acyl migrations in  $\beta,\gamma$ -unsaturated ketones. in *CRS Handbook of Organic Photochemistry and Photobiology*, ed. W. Horspool and F. Lensi, CRS Press, 2nd edn, 2004, ch. 79, no. 1, p. 79.
- (a) M. D'Auria and R. Racioppi, *Molecules*, 2013, **18**, 11384; (b) M. Fréneau and N. Hoffmann, *J. Photochem. Photobiol., C*, 2017, **33**, 83; (c) M. D'Auria, *Photochem. Photobiol. Sci.*, 2019, **18**, 2297.
- (a) N. Hoffmann, *Chem. Rev.*, 2008, **108**, 1052; (b) T. Bach and J. P. Hehn, *Angew. Chem., Int. Ed.*, 2011, **50**, 1000; (c) M. D. Kärkäs, J. A. Porco and C. R. J. Stephenson, *Chem. Rev.*, 2016, **116**, 9683.
- For recent publications, see: (a) R. A. Valiulin, T. M. Arisco and A. G. Kutateladze, *J. Org. Chem.*, 2013, **78**, 2012; (b) C.-C. Wang, Y.-C. Ku and G. J. Chuang, *J. Org. Chem.*, 2015, **80**, 10979; (c) E. Kumarasamy, R. Raghunathan, S. K. Kandappa, A. Sreenithya, S. Jockusch, R. B. Sunoj and J. Sivaguru, *J. Am. Chem. Soc.*, 2017, **139**, 655; (d) Q. Yan,

- B. Bolte, Y. Bai, M. G. Banwell, A. C. Willis and P. D. Carr, *J. Org. Chem.*, 2017, **82**, 8008; (e) J. Emsermann and T. Opatz, *Eur. J. Org. Chem.*, 2017, 3362; (f) R. Sahu and V. Singh, *Tetrahedron*, 2017, **73**, 6515; (g) J. Buendia, Z. Chang, H. Eijlsberg, R. Guillot, A. Frongia, F. Secci, J. Xie, S. Robin, T. Boddaert and D. J. Aitken, *Angew. Chem., Int. Ed.*, 2018, **57**, 6592; (h) P. Lan, M. G. Banwell and A. C. Willis, *Org. Lett.*, 2015, **17**, 166.
- 6 (a) J. Iriondo-Alberdi, J. E. Perea-Buceta and M. F. Greaney, *Org. Lett.*, 2005, **7**, 3969; (b) D.-S. Hsu, Y.-Y. Chou, Y.-S. Tung and C.-C. Liao, *Chem. – Eur. J.*, 2010, **16**, 3121; (c) H. P. Pepper, K. K. W. Kuan and J. H. George, *Org. Lett.*, 2012, **14**, 1524.
- 7 T. Tsuno and K. Sugiyama, *Heterocycles*, 2002, **57**, 2129.
- 8 (a) B. Satpathi, L. Dutta and S. S. V. Ramasastry, *Org. Lett.*, 2019, **21**, 170; (b) R. Liang, K. Chen, Q. Zhang, J. Zhang, H. Jiang and S. Zhu, *Angew. Chem., Int. Ed.*, 2016, **55**, 2587; (c) C. Liu and Y. K. Liu, *J. Org. Chem.*, 2017, **82**, 10450; (d) J. C. Morris and C. S. P. McErlean, *Org. Biomol. Chem.*, 2016, **14**, 1236; (e) M. Wu, J. Yang, F. Luo, C. Cheng and G. Zhu, *Org. Biomol. Chem.*, 2019, **17**, 5684.
- 9 V. Lokshin and V. Khodorkovsky, *Tetrahedron*, 2018, **74**, 418 and references therein.
- 10 (a) P. Qian, B. Du, R. Song, X. Wu, H. Mei, J. Han and Y. Pan, *J. Org. Chem.*, 2016, **81**, 6546; (b) H. Xu, F. Sha, Q. Li and X.-Y. Wu, *Org. Biomol. Chem.*, 2018, **16**, 7214; (c) J. Duan, Y. Cheng, R. Li and P. Li, *Org. Chem. Front.*, 2016, **3**; (d) Y. Han, Y. Zhu, P. Zhang, W. Li and P. Li, *Chemistry-Select*, 2017, **2**, 11380; (e) Y.-H. Jiang, J. Sun, Q. Sun and C.-G. Yan, *Asian J. Org. Chem.*, 2017, **6**, 862; (f) J. K. Yu, H. W. Chien, Y. J. Lin, P. Karanam, Y. H. Chen and W. Lin, *Chem. Commun.*, 2018, **54**, 9921; (g) J. Qi, J. Zheng and S. Cui, *Org. Chem. Front.*, 2018, **5**, 222; (h) W.-J. Yang, H.-L. Fang, J. Sun and C.-G. Yan, *ACS Omega*, 2019, **4**, 13553–13569; (i) R. Ye and C.-G. Yan, *Eur. J. Org. Chem.*, 2019, 5882; (j) A. S. Filatov, S. Wang, O. V. Khoroshilova, S. V. Lozovskiy, A. G. Larina, V. M. Boitsov and A. V. Stepanov, *J. Org. Chem.*, 2019, **84**, 7017.
- 11 R. Samineni, P. Srihari and G. Mehta, *Org. Lett.*, 2016, **18**, 2832.
- 12 Q. Yao, L. Kong, M. Wang, Y. Yuan, R. Sun and Y. Li, *Org. Lett.*, 2018, **20**, 1744.
- 13 B. Furth, G. Daccord and J. Kossanyi, *Tetrahedron Lett.*, 1975, **48**, 4259.
- 14 T. Kirschberg and J. Mattay, *J. Org. Chem.*, 1996, **61**, 8885.
- 15 T. Imai and S. Nishida, *Can. J. Chem.*, 1981, **59**, 2503.
- 16 G. Adames, C. Bibby and R. Grigg, *Chem. Commun.*, 1972, 491.
- 17 (a) R. A. Valiulin and A. G. Kutateladze, *Org. Lett.*, 2009, **11**, 3886; (b) R. A. Valiulin, T. M. Arisco and A. G. Kutateladze, *J. Org. Chem.*, 2013, **78**, 2012.
- 18 R. Pérez-Ruiz, M. A. Miranda, R. Alle, K. Meerholz and A. G. Griesbeck, *Photochem. Photobiol. Sci.*, 2006, **5**, 51.
- 19 S.-H. Wu, D.-G. Wu and Y.-W. Chen, *Chem. Biodiversity*, 2010, **7**, 90.
- 20 J. Yu, J. A. Elix and M. N. Iskander, *Phytochemistry*, 1990, **29**, 3859.
- 21 T. Bach, M. Kemmler and E. Herdtweck, *J. Org. Chem.*, 2003, **68**, 1994.
- 22 P. Lu and T. Bach, *Angew. Chem., Int. Ed.*, 2012, **51**, 1261.
- 23 P. Lu, E. Herdtweck and T. Bach, *Chem. – Asian J.*, 2012, 1947.
- 24 (a) S. J. Piao, Y. L. Song, W. H. Jiao, F. Yang, X. F. Liu, W. S. Chen, B. N. Han and H. W. Lin, *Org. Lett.*, 2013, **15**, 3526; (b) S. A. Ruider, T. Sandmeier and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2015, **54**, 2378.
- 25 (a) J. Marrero, A. D. Rodríguez, P. Baran, R. G. Raptis, J. A. Sánchez, E. Ortega-Barria and T. L. Capson, *Org. Lett.*, 2004, **6**, 1661; (b) R. A. Craig and B. M. Stoltz, *Chem. Rev.*, 2017, **117**, 7878.
- 26 H.-S. Yeom, H. Li, Y. Tang and R. P. Hsung, *Org. Lett.*, 2013, **15**, 3130.
- 27 F. Birbaum, A. Neels and C. G. Bochet, *Org. Lett.*, 2008, **10**, 3175.
- 28 Q. Liu, J. Wang, D. Li, G. L. Gao, C. Yang, Y. Gao and W. Xia, *J. Org. Chem.*, 2017, **82**, 7856.
- 29 X. Zhang, *J. Mol. Model.*, 2019, **25**, 14.
- 30 (a) Y. Inoue, S. Hagiwara, Y. Daino and T. Hakushi, *J. Chem. Soc., Chem. Commun.*, 1985, 1307; (b) W. Fuß, S. Panja, W. E. Schmid and S. A. Trushin, *Mol. Phys.*, 2006, **104**, 1133.