ORGANIC
LETTERS

2011
Vol. 13, No. 3
474−477

Photoinduced Rearrangements of 3,3′-Bis(arylbenzofurans)

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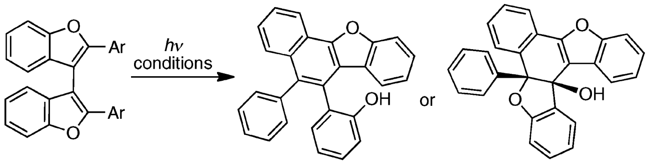
Received November 19, 2010

ABSTRACT



1a **2a** **3**

Complex tetracyclic ring systems were assembled by a photoinduced rearrangement of 3,3′-bis(arylbenzofurans). Irradiation of 1 under N_2 atmosphere yielded the benzonaphthofurans 2 in 75−90% yield. When the reaction was conducted under an O_2 atmosphere in the presence of tetracyanoethylene (TCNE) a different reaction pathway was observed leading to the isolation of 3 as the major product. Also, the photochemical properties of these novel structures were investigated.

Light has always been regarded as a powerful energy source for chemists to perform reactions.[1] Electronic excitation changes the distribution of electrons in the molecules affecting their chemical properties, which can lead sometimes to novel and unexpected reactivities. Typical compounds obtained from UV or visible light irradiation are polycyclic or highly functionalized molecules. Such new products formed by irradiation would be difficult to access with standard chemistry reactions of ground state substrates. Nowadays, the field of organic photochemical reactions experiences a veritable revival of activity in both academics and industry,[2] in particular with its use in the context of green chemistry or total synthesis.[3]

Among the polycyclic aromatic molecules, which are substrates of interest for photochemistry, benzofuran derivatives have attracted considerable attention on their photoluminescent properties due to their conjugated π-system.[4] Hence, the use of benzofurans for functional materials became a rich field of investigations. Applications have been reported as photochromic compounds and dyes.[5] Noteworthy is the recent use of benzofuran trimers as materials for organic electroluminescence.[6] We lately developed a quick and easy way to access dimeric derivatives of benzofurans via a gold-catalyzed domino process.[7] The new 3,3′-bisbenzofurans obtained following this procedure are interesting substrates for photochemical reactions. During our investigations on their photoluminescent properties we

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(1) Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1193.
(2) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052.

(3) Ciana, C.-L.; Bochet, C. G. *Chimia* **2007**, *61*, 650. For recent selected examples see: (a) Ravelli, D.; Zema, M.; Mella, M.; Fagnoni, M.; Albini, A. *Org. Biomol. Chem.* **2010**, *8*, 4158. (b) Fasani, E.; Manet, I.; Capobianco, M. L.; Monti, S.; Pretali, L.; Albini, A. *Org. Biomol. Chem.* **2010**, *8*, 3621. (c) Fleck, M.; Bach, T. *Chem.*−*Eur. J.* **2010**, *16*, 6015. (d) Jahjah, R.; Gassama, A.; Bulach, V.; Suzuki, C.; Abe, M.; Hoffmann, N.; Martinez, A.; Nuzillard, J.-M. *Chem.*−*Eur. J.* **2010**, *16*, 3341. (e) Dichiarante, V.; Fagnoni, M.; Albini, A. *Green Chem.* **2009**, *11*, 942. (f) Selig, P.; Herdtweck, E.; Bach, T. *Chem.*−*Eur. J.* **2009**, *15*, 3509. (g) Griesbeck, A. G.; Neudörfl, J.; Hörauf, A.; Specht, S.; Raabe, A. *J. Med. Chem.* **2009**, *52*, 3420. (h) Vogt, F.; Jödicke, K.; Schröder, J.; Bach, T. *Synthesis* **2009**, 4268. (i) Débieux, J. L.; Bochet, C. G. *J. Org. Chem.* **2009**, *74*, 4519. (j) Zimmerman, H. E.; Shorunov, S. *J. Org. Chem.* **2009**, *74*, 5411. (k) Fleck, M.; Bach, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 6189. (l) Guthmann, H.; Könemann, M.; Bach, T. *Eur. J. Org. Chem.* **2007**, 632. (m) Bauer, A.; Westkämper, F.; Grimme, S.; Bach, T. *Nature* **2005**, *436*, 1139.
(4) (a) Yamaguchi, T.; Takami, S.; Irie, M. *J. Photochem. Photobiol., A* **2008**, *193*, 146. (b) Sakamoto, M.; Kinbara, A.; Yagi, T.; Mino, T.; Yamaguchi, K.; Fujita, T. *Chem. Commun.* **2000**, 1201.
(5) (a) Škoriæ, I.; Ciorba, S.; Spalletti, A.; Šindler-Kulyk, M. *J. Photochem. Photobiol., A* **2009**, *202*, 136. (b) Piloto, A. M.; Fonseca, A. S. C.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron* **2006**, *62*, 9258. (c) Piloto, A. M.; Costa, S. P. G.; Gonçalves, M. S. T. *Tetrahedron Lett.* **2005**, *46*, 4757.
(6) Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem.*−*Eur. J.* **2004**, *10*, 518.
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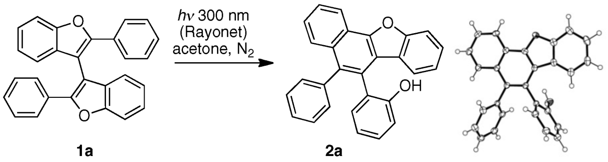
10.1021/ol102816a

observed photorearrangements on 3,3′-bis(arylbenzofurans) under UV irradiation leading to the formation of different benzonaphthofuran derivatives depending on the reaction conditions used.

First observations revealed the relative reactivity of such compounds when submitted to a UV light source: irradiation of derivative **1a** gave rise to the formation of benzonaphthofuran **2a** mainly (Scheme 1). The structure of compound **2a** has been confirmed by a single-crystal X-ray analysis (The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 798480. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html).

Scheme 1. Photorearrangement of Dimer **1a**



Optimization of the process was performed with **1a** as substrate. Different sources of ultraviolet irradiation were used: UV TLC lamp,[8] UV monochromator,[9] Rayonet UV reactor,[10] in combination with different wavelengths (from 300 to 365 nm); several solvents were also tested (chloroform, acetonitrile, benzene, dimethylsulfoxide, acetone). Screening of conditions on NMR scale experiments showed that the appropriate atmosphere of the reaction is crucial since aerobic conditions led to lower formation of **2a**. Finally, running the reaction under inert atmosphere in anhydrous acetone within a Rayonet reactor (300 nm) at 40 °C led to the isolation of the photorearrangement compound **2a** in 88% yield.

We prepared the 3,3′-bis(arylbenzofurans) **1b**–**e** according to the previously published method[7](Scheme 2) and subjected them to the optimized reaction conditions, which led to the formation of the corresponding photorearrangement compounds **2b**–**e** (Table 1). The reaction is not affected by the nature of the starting material since the different compounds have been obtained with high yields between 75% and 90%. The presence of substituents at the para position of the 3,3′-bis(arylbenzofurans) was tolerated for the photorearrangement independently of their electron-donating or electron-withdrawing effect (entries 2–4, Table 1). The photoreaction is also not prevented by the presence of an electron-donating group (methoxy) on the benzofuran moiety (entry 5, Table 1).[11]

Scheme 2. Domino Process Toward the Formation of 3,3′-Bis(arylbenzofurans) **1**

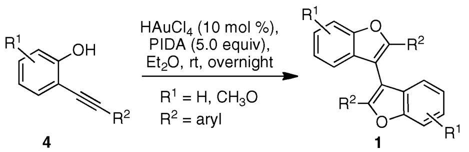
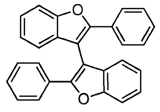
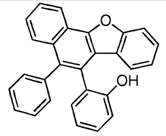
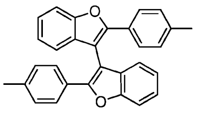
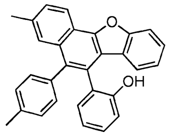
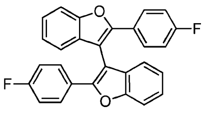
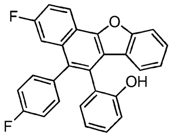
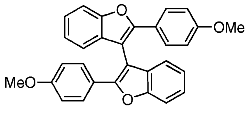
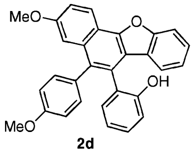
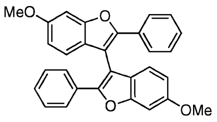
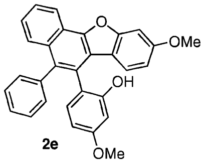


Table 1. Substrate Scope of the Photorearrangement on 3,3′-Bis(arylbenzofurans) **1a**–**e**[a]

entry	starting material	product	yield[b]
1	 **1a**	 **2a**	88%
2	 **1b**	 **2b**	75%
3	 **1c**	 **2c**	82%
4	 **1d**	 **2d**	90%
5	 **1e**	 **2e**	80%

[a] Reaction conditions: **1**, anhydrous acetone (0.02–0.03 mol·L^{-1}), 300 nm irradiation (Rayonet), N$_2$ atmosphere, 18 h, 40 °C. [b] Isolated yields.

During the course of improving the formation of **2a**–**e**, we tested the introduction of photosensitizers to see whether or not their use would increase the reaction yields. Several sensitizers were employed: rose Bengal, benzophenone, tetracyanoethylene, and maleic anhydride. Surprisingly, the presence of tetracyanoethylene (TCNE) in the acetone solution of dimer **1a** led under ultraviolet irradiation (300 nm) to the formation of a new compound **3** (Scheme 3).

Unambiguous assignment of all ^{1}H and ^{13}C resonances of **3** was achieved by one- and two-dimensional NMR experiments (selective TOCSY, COSY, HMQC, and HMBC

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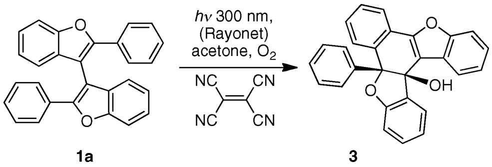
(8) UV lamp 254/302/365 nm, UVProducts.

(9) UV Monochromator, Polychrome V, Till Photonics.

(10) Rayonet reactor RPR-100, Southern New England Ultra Violet Company, 270/300/350 nm.

(11) Similar benzonaphthofurans have been synthesized recently by the halopalladation/decarboxylation/carbon–carbon bond forming domino process in moderate to good yields: Huang, X.-C.; Wang, F.; Liang, Y.; Li, J.-H. *Org. Lett.* **2009**, *11*, 1139.

Scheme 3. Photorearrangement of Dimer **1a** in the Presence of Tetracyanoethylene (TCNE)



spectra). The structure of the new compound could be determined by using NOESY techniques. According to the analytical data, only one diastereomer of **3** was formed during the reaction installing two stereocenters stereospecifically. Although only one diastereomer could be isolated the yield of 32% does not exclude the formation of the other diastereomer. Interestingly, no formation of **3** was observed when other photosensitizers were used. Moreover, no reaction occurred between tetracyanoethylene and **1a** in the absence of UV irradiation. The atmosphere of the reaction seemed to be a crucial point since the formation of **3** was improved under oxygen atmosphere. Optimization for the formation of compound **3** led to a yield of 32% (Table 2).

Table 2. Screening of the Conditions Toward the Formation of **3**[a]

entry	irradiation	atmosphere	time, h	**3** yield,[b] %
1	UV lamp, 302 nm	air	2	8
2	Rayonet, 300 nm	O_2	4	19
3	Rayonet, 300 nm	O_2	18	32

[a] Reaction conditions: **1**, TCNE (10 equiv), anhydrous acetone (0.02−0.03 mol·L^{-1}). [b] Isolated yields.

Taking into account that the formation of **3** was done in the presence of a sensitizer (tetracyanoethylene) and improved by oxygen atmosphere, it would be reasonable to assume a photo-oxygenation of **1a** and the involvement of singlet oxygen.[12,13] However, in this case, another sensitizer producing singlet oxygen should also lead to product **3** formation, which is not observed.

A proposed mechanism for the formation of **2a** and **3** is depicted in Figure 1. A common step for the two pathways is the conrotatory 6π-photocyclization of **1a** leading to intermediate **A** with the creation of a new six-membered ring (after irradiation at 302 nm for 2 min a new transient species with an absorption maximum at 510 nm was observed in the UV spectrum). Under N_2 atmosphere the cleavage of one furan ring via a *syn*-elimination occurs and releases **2a**. On the other hand, in the presence of TCNE an electron tranfer can be envisioned leading to the radical cation of **A**, which then deprotonates to form a radical intermediate **B**. This reacts with O_2 from the less hindered convex face to peroxo-compound **C**, which finally turns into **3** after trapping of the peroxo by tetracyanoethylene (tetracyanoethylene epoxide formation was osberved on crude NMR).[14] Absorption and fluorescence spectra have been measured for derivatives **2a**−**e** and **3**. The measurements have been performed on degassed solutions of **2a**−**e** and **3** (1×10^{-5} M in dichloromethane). Compounds **2a**−**e** exhibited an UV absorption maximum centered around 270 nm for all the compounds showing a weak impact of the nature of the substituents (Figure 2). Despite the more extended π-system in the products compared to the starting material, an hypsochromic effect is observed for compounds **2a**−**e** by comparison with the 3,3′-bis(arylbenzofurans) **1a**−**e**, which presented a maxi-

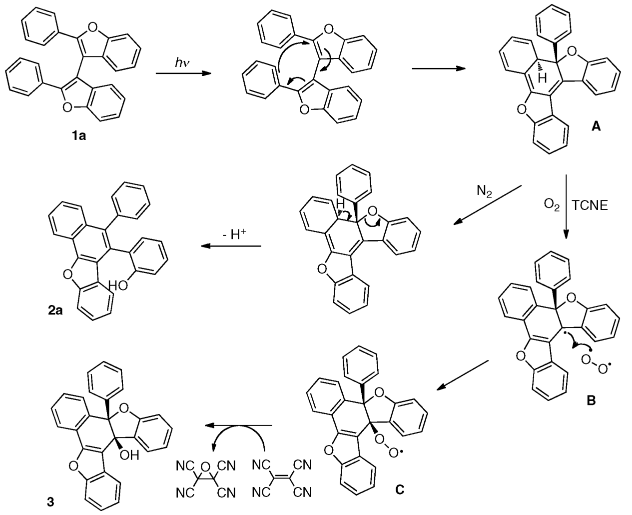


Figure 1. Proposed mechanism for the formation of **2a** and **3**.

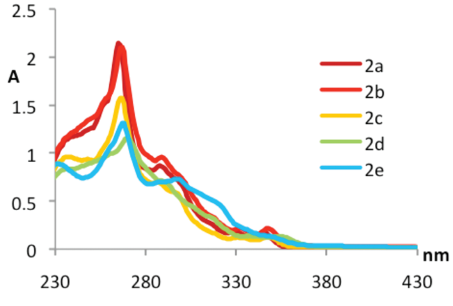


Figure 2. UV spectra of compounds **2a**−**e** in dichloromethane.

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(12) (a) Clennan, E. L. *Tetrahedron* **2000**, *56*, 9151. (b) Prein, M.; Adam, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 477. (c) Prein, M.; Adam, W. *Acc. Chem. Res.* **1996**, *29*, 275. (d) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685. (e) For examples of organic chemistry of singlet oxygen see: *Tetrahedron* **2006**, *62*, 46.

(13) (a) Clenann, E. L. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Vol. 12, Synthetic Organic Photochemistry; Griesbeck, A. G., Mattay, J., Eds.; Marcel Dekker: New York, 2005; p 365. (b) Stratakis, M.; Orfanopoulos, M. *Tetrahedron* **2000**, *56*, 1595. (c) Adam, W.; Wirth, T. *Acc. Chem. Res.* **1999**, *32*, 703.

(14) (a) Miller, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2508. (b) Linn, W. J. *Org. Synth.* **1969**, *49*, 103.

mum between 302 and 327 nm. Compound **3**, on the other hand, showed a small bathochromic effect with a maximum absorption at 320 nm (Figure 3).

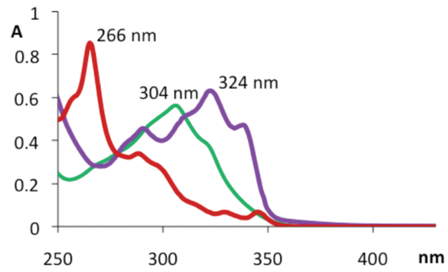

Figure 3. Comparative UV spectra of **1a** (green), **2a** (red), and **3** (purple) in dichloromethane.

This could be explained by the cross-conjugated chromophore nature of compounds **1a**−**e**.[15] This phenomena is observed for certain oligomeric and polymeric systems[16] and notably for indigo dyes where the inherent cross-conjugation has been shown responsible for the high bathochromicity of these π-systems.[17]

The fluorescence responses of **2a**−**e** exhibited a quite similar curve shape meaning that the nature of the substituents on the aryl moieties also has low impact on emission properties of these compounds. Fluorescence of compound **3** was found to be very weak; this is explained most likely by the smaller conjugated π-system present in the molecule compared to its analogue **2a** (Figure 4).

In summary, we have investigated the photochemical and photoluminescent properties of 3,3′-bis(arylbenzofurans). Compounds **1** can be efficiently converted to the benzonaphthofurans **2**. We have shown that the photoreactivity is dependent on the presence/absence of additive and on the nature of the reaction atmosphere. In the presence of O_2 and TCNE **3** was isolated as the mayor product in a side reaction, which is formed via a different mechanism. The benzonaphthofuran derivatives obtained present a potentially interesting backbone for bioactive molecules given the large range of biological applications exhibited by benzofurans and dibenzofurans of which they are closely related.[18] In the future, the reaction will be applied to synthesize derivatives with interesting photoluminescent or biological properties.

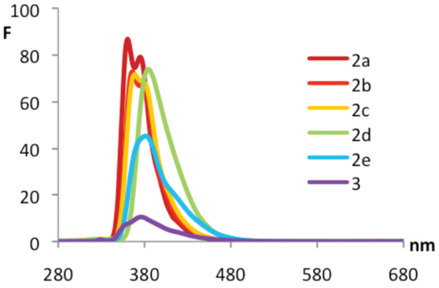

Figure 4. Fluorescence spectra of compounds **2a**−**e** and **3** in dichloromethane.

Acknowledgment. The authors thank Prof. Dr. Bernd Giese, University of Fribourg (Switzerland), for stimulating discussions. M.A. thanks the Roche Research Foundation and the Novartis Foundation for financial support. H.A.W. is indebted to the Fonds der Chemischen Industrie for a Liebig Fellowship. Umicore and Johnson Matthey are gratefully acknowledged for generously providing auric acid.

Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL102816A

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