Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 64 (2008) 3928−3934
www.elsevier.com/locate/tet

Photobehaviour of 2- and 3-heteroaryl substituted *o*-divinylbenzenes; formation of fused 2,3- and 3,2-heteroareno-benzobicyclo[3.2.1]octadienes and 3-heteroaryl benzobicyclo[2.1.1]hexenes

Dragana Vidaković [a], Irena Škorić [a], Margareta Horvat [a], Željko Marinić [b], Marija Šindler-Kulyk [a,*]

[a] *Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia*
[b] *NMR Center, Rudjer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

Received 12 November 2007; received in revised form 1 February 2008; accepted 21 February 2008
Available online 26 February 2008

Dedicated to Professor Douglas C. Neckers on the occasion of his 70th birthday

---

Abstract

New β-3-thienyl (**8**) and β-3-furyl derivatives of *o*-divinylbenzene (**9**) have been synthesised and their photochemical behaviour compared with 2-thienyl (**7**) and 2-furyl derivatives (**2**). Whereas the β-(2-heteroaryl) substituted *o*-divinylbenzenes (**7** or **2**) give only bicyclo[3.2.1]octadiene structure (**14** or **1**) by 1,6-ring closure of the biradical intermediate, β-(3-heteroaryl) substituted *o*-divinylbenzenes (**8** or **9**) give bicyclo[3.2.1]octadiene structure (**23** or **24**) and bicyclo[2.1.1]hexene structure (**25** or **26**) by 1,6- and 1,4-ring closure, respectively. This photochemical approach provides a simple method to 2,3- and 3,2-fused thiophene and furan polycyclic compounds.

© 2008 Elsevier Ltd. All rights reserved.

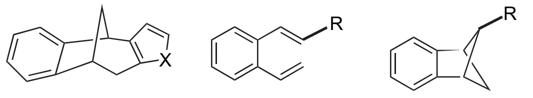
Keywords: Oxygen heterocycles; Sulfur heterocycles; Furan; Thiophene; Photochemistry; Photocycloaddition; Synthesis

---

1. Introduction

There is an increasing interest in the bicyclo[3.2.1]octane structures since they represent the basic framework of numerous important biologically active natural compounds or their metabolites. Their skeleton has also proved to be useful reactive intermediate in various stereoselective transformations making these derivatives powerful building blocks in organic synthesis.[1] In one of our previous papers[2] on the photochemistry of styryl substituted furan derivatives[2−12] we demonstrated for the first time the photochemical approach to furano-fused bicyclo[3.2.1]octadiene structure (**1**) by simple irradiation of 2-(*o*-vinylstyryl)furan (**2**) (Fig. 1). On the other hand, their nitrogen analogues, pyrrole derivatives (**3**),[13−20] gave completely different photoproducts. It was found that only alkoxycarbonyl substituted pyrrole derivatives[21] gave pyrrolo-fused benzobicyclo[3.2.1]octadiene structure (**4**). In the case of 2-(*o*-vinylstyryl)furans with the substituent in position 3 of the furan ring (**5**) formation of the bicyclo[2.1.1]hexene structure (**6**) was observed,[9] presumably due to the steric reasons.

In continuation of our interest for the effect of heteroatoms, as well as their position in the heteroaromatic ring on the



1: X=O
4: X=NCOOR

2: R=2-furyl
3: R=2-pyrrolyl
5: R=2-(3-X)furyl
7: R=2-thienyl
8: R=3-thienyl
9: R=3-furyl
10: R=phenyl

6: R=2-(3-X)furyl
11: R=phenyl

Figure 1.

---

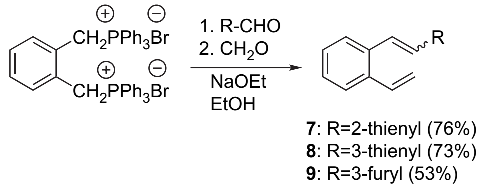
* Corresponding author. Tel.: +385 1 4597242; fax: +385 1 4597250.
E-mail address: marija.sindler@fkit.hr (M. Šindler-Kulyk).

0040-4020/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.02.062

formation of heteropolycyclic compounds, we present here for the first time the photochemical behaviour of thiophene derivatives (**7**, **8**) and furan derivative (**9**). We anticipated that introduction of sulfur as heteroatom, by replacing the furan moiety with the thiophenes, may have influence on the excited state properties of this new hexatriene system and as a consequence the formation of diverse photoproducts. Based solely on the aromaticity of heterocycles,[22,23] the thiophene being more aromatic than furan, it might be expected that thiophene derivative **7** resembles the photochemical behaviour of its parent benzene derivative **10**, which upon irradiation closes to bicyclo[2.1.1]hexene **11**.[24–28]

2. Results and discussion

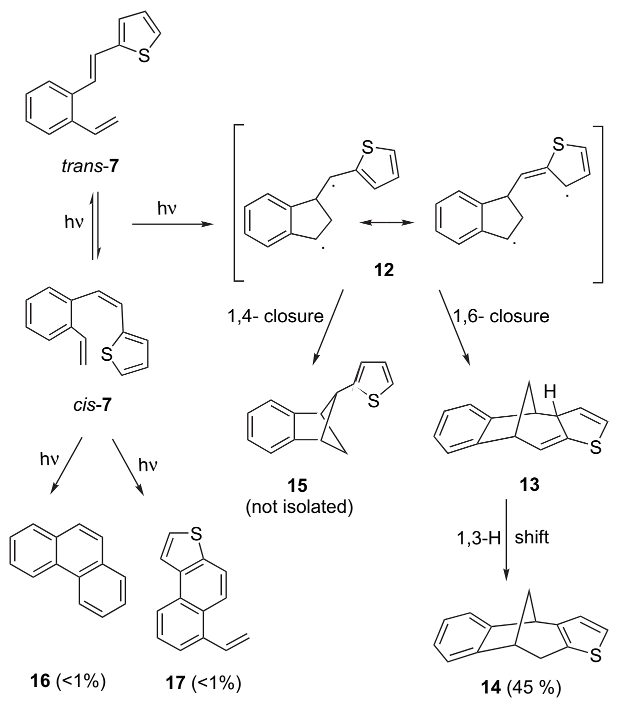
Starting compounds, 2-[2-(2-ethenylphenyl)ethenyl]thiophene (**7**),[3] 3-[2-(2-ethenylphenyl)ethenyl]thiophene (**8**) and 3-[2-(2-ethenylphenyl)ethenyl]furan (**9**) were synthesised in a good to very good yields (50–85%) by the Wittig reaction of β,β-*o*-xylyl(ditriphenylphosphonium) dibromide and the corresponding aldehydes (Scheme 1) according to the general procedure described for the β-heteroaryl-*o*-divinylbenzenes.[3] They were obtained as mixtures of trans- (60–70%) and cis-isomer (30–40%) that were separated by column chromatography and characterised spectroscopically.



Scheme 1.

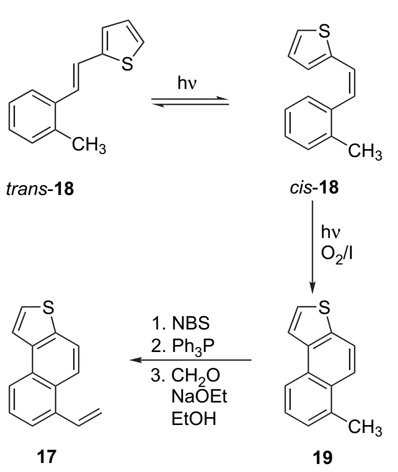
The irradiation experiments were performed under anaerobic conditions and in petroleum ether as a solvent. On irradiation of 2-thienyl substituted *o*-divinylbenzene **7** (Scheme 2) the thieno-fused benzobicyclo[3.2.1]octadiene **14** was isolated as the main product in 45% yield. In addition, minor quantities of phenanthrene (**16**) and vinylnaphthothiophene (**17**) were found in the first fractions during the column chromatography and the high-molecular-weight products remained on the column.

The photoproducts are easily identified by their NMR spectra, using one- and two-dimensional NMR techniques, and their comparison with the spectra of photoproducts, previously obtained on irradiation of 2-[2-(2-ethenylphenyl)ethenyl]furan (**2**).[2] The proposed mechanism for the formation of the main product, bicyclo[3.2.1]octadiene derivative **14**, as in the case of furan derivative **2**,[2] involves intramolecular cycloaddition via biradical intermediate **12** followed by preferred 1,6-ring closure to **13** and subsequent 1,3-H shift. The 2-thienyl-bicyclo[2.1.1]hexene derivative **15**, which could be formed by 1,4-ring closure of **12**, was not detected. The 1,4-ring closure was also not observed on irradiation of 2-[2-(2-ethenylphenyl)-ethenyl]furan (**2**)[2,4,8,9] contrary to the photochemical properties of the corresponding phenyl analogous **10**, *o*-vinylstilbene,[24,25] where the main product was the phenyl-benzobicyclo[2.1.1]hexene **11**.



Scheme 2.

Formation of byproducts **16** and **17** can occur from the cis-configuration of **7** by two different mechanisms: the intramolecular photoinduced [4+2] cycloaddition followed by elimination of H_2S produces phenanthrene (**16**)[29] while photochemical electrocyclization process leads to vinylnaphthothiophene **17**. The presence of phenanthrene (**16**) was confirmed by comparison of its ^{1}H NMR spectrum with the ^{1}H NMR spectrum of authentic sample. The structure of new 6-vinylnaphtho[2,1-*b*]thiophene (**17**), formed in too small quantities to be analysed completely, was confirmed by its independent synthesis. The vinylnaphthothiophene derivative **17** was prepared by photochemical ring closure of **18** to **19** followed by a sequence of reactions according to Scheme 3.



Scheme 3.

Download English Version:

https://daneshyari.com/en/article/5225748

Download Persian Version:

https://daneshyari.com/article/5225748

Daneshyari.com