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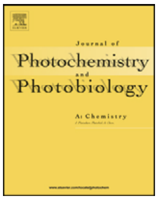

Photochemistry of ω-(*o*-vinylphenyl)-ω′-(phenyl/2-furyl) butadienes: New approach to 4-substituted benzobicyclo[3.2.1]octadienes

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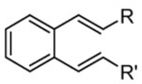
ABSTRACT

Novel 1-(*o*-vinylphenyl)-4-(phenyl/2-furyl) butadienes (**4a**,**b**), synthesized in one step, undergo intramolecular photocycloaddition reaction to benzobicyclo[3.2.1]octadiene derivatives (**6a**,**b**) in very good yield (70–90%). In the case of phenyl derivative (**4a**) only *endo*-phenyl-benzobicyclo[3.2.1]octadiene isomer (*endo*-**6a**) was isolated whereas the furan (**4b**) derivative resulted in a mixture of *endo*- and *exo*-bicyclic isomer (**6b**). Phenyl benzobicyclo[3.2.1]octadiene derivative (*endo*-**6a**) underwent further di-π-methane rearrangement leading to tricyclic structure (*endo*-**7a**). The isolated compound **6a** and the product of the rearrangement *endo*-**7a** were characterised by X-ray structure analysis.

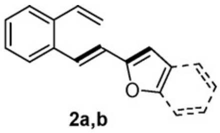
1. Introduction

Synthetic organic photochemistry accasionally provides an easy access to complicated structures, difficult to obtain by a classical synthetic approach [1]. Among the most studied and used reactions are the intra- and intermolecular photocycloadditions [2]. In order to prepare new hetero-polycyclic compounds this methodology was used by us studying the photochemical behavior of β- or β,β′-substituted *o*-divinylbenzenes, i.e. heteroaryl substituted hexatrienes **1** with the central double bond incorporated into the benzene ring. Since our first report [3] on the intramolecular photocycloaddition reaction of *o*-vinyl substituted furostilbene **2a** and formation of benzo-furo fused bicyclo[3.2.1]octadiene structure **3a**, many results about the photochemical behaviour of *o*-vinyl substituted heteroaryl stilbene analogues **1** (heteroarene moiety = furan [4–15], pyrrole [16–23], thiophene [4,5], sydnone [24,25]) have been obtained.

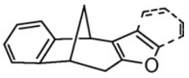


1

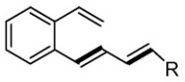
R = H; R' = furan, pyrrole, thiophene, sydnone
R = R' = furan, pyrrole, thiophene



2a,b



3a,b



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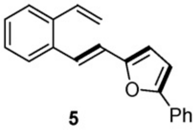

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The formation of benzobicyclo[3.2.1]octadiene structure **3a** includes initial five membered ring closure of **2a** followed by 1,6-closure through the participation of the furan double bond [3]. In the case of benzofuran derivative **2b** this process is even cleaner and more pronounced leading to the benzofuran-fused [3.2.1] bicyclic structure **3b** [13]. We imply that the substituted butadiene **4**, the vinylogue of divinylbenzene, could react similarly as **2a** and/or **2b** and give intramolecular cycloadduct. It should be mentioned that phenyl substituted furan derivative **5** gave upon irradiation [15] mainly high-molecular-weight products, besides only traces of substituted bicyclic structure **3a**.

As a part of our continuing interest in the photochemistry of conjugated systems we extended our research to new *o*-vinylphenyl

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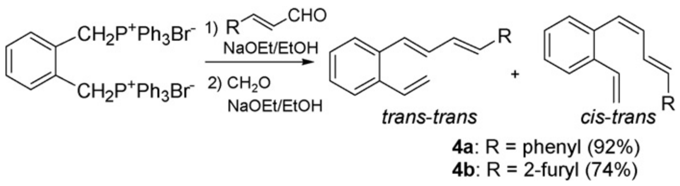

Scheme 1.

substituted butadienes **4** as substrates for photochemical transformations to benzobicyclo[3.2.1]octadiene skeleton [26–29], easily derivatised to saturated structures with various functionalities. The photoisomerization reactions [30–39] as well as some electrocyclisation reactions [40,41] of 1,4-diphenyl butadienes are studied but to the best of our knowledge no intramolecular photocycloadditions of their vinylogues are known. In this paper, we describe for the first time, one-step photochemical transformations of novel *o*-butadienylstyrenes **4**, octatetraenes with one double bond incorporated into the benzene ring.

2. Results and discussion

The starting materials, 1-(*o*-vinylphenyl)-4-(phenyl/2-furyl substituted) butadienes (**4a**,**b**) were prepared by the Wittig reaction from β,β′-*o*-xylyl(ditriphenylphosphonium)dibromide and corresponding aldehydes (Scheme 1) in good yields (74–92%) as mixtures of *cis*,*trans*- and *trans*,*trans*-isomers, according to the procedure described in previous papers for the heteroarylstilbene analogues [42].

According to ^{1}H NMR spectra of the crude reaction mixtures the ratio of *trans*,*trans*- to *cis*,*trans*-isomers was very similar in both derivatives (~3:2). The isomers of **4a**,**b** were separated combining column chromatography and thin layer chromatography on silica gel and identified spectroscopically.

The UV spectra (Fig. 1) of separated *cis*,*trans*- and *trans*,*trans*-**4a** and **4b**, respectively, clearly show the substituent and configurational influence on absorption characteristics. The *trans*,*trans*-**4a**,**b** isomers show a bathochromic shift and an increase of the molar absorption coefficients in comparison to their *cis*,*trans*-isomers, as expected, because of increased molecular planarity of *trans*,*trans* configurations and the possibility of better delocalisation of π-electrons.

The phenyl derivatives, *trans*,*trans*-**4a** (Fig. 2) and *cis*,*trans*-**4a** (Fig. 3) were irradiated and the reaction course followed by taking the UV spectra at indicated times. It is evident from the absorption spectra that photoisomerization is the primary process followed by competitive photochemical reaction. It is difficult to discuss about the composition of the photostationary mixture because of unsymmetrical structure of **4a** and possibility of existence and interconversion of four isomers: *trans*,*trans*-, *trans*,*cis*-, *cis*,*trans*- and *cis*,*cis*-**4a**.

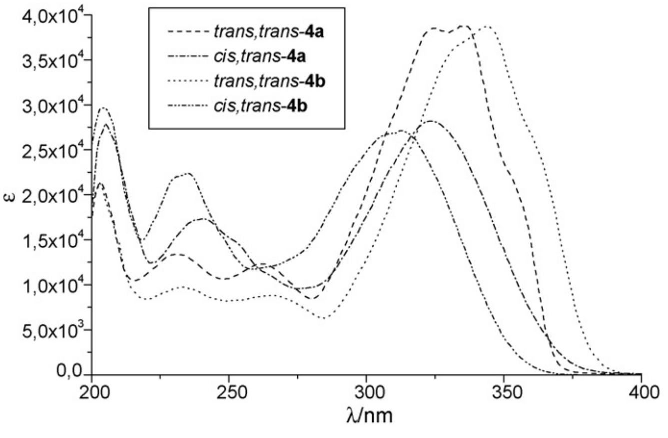

Fig. 1. UV spectra of *trans*,*trans*- and *cis*,*trans*-**4a**,**b** in EtOH.

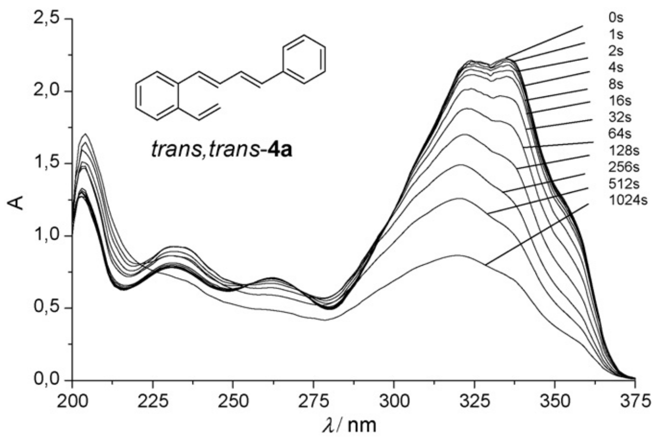

Fig. 2. The irradiation of *trans*,*trans*-**4a** followed by taking the UV spectra at indicated times.

The irradiation experiments of **4a**,**b** were performed in petroleum ether solutions under anaerobic conditions at 300 and 350 nm, giving in all cases *endo*-4-substituted benzobicyclo[3.2.1]octadienes **6a** or **6b**, respectively, as the main product (Scheme 2).

It is interesting to note that in the case of phenyl derivative **4a** only *endo*-isomer **6a** was isolated while the furyl derivative **4b** gave a mixture of *endo*- and *exo*-isomers **6b** in the ratio 3:1. On irradiation of phenyl derivative **4a** at 300 nm to full conversion of the starting material, besides *endo*-**6a** new compound *endo*-**7a** was isolated. In the case of furyl derivative **4b**, irradiated under the same conditions, no structure corresponding to *endo*-**7a** was observed, besides some tarry material. The photoproducts (*endo*-**6a**, *endo*-**6b**, *exo*-**6b**, *endo*-**7a**) were separated by column chromatography on silica gel and the structures deduced unequivocally from spectral studies.

From the ^{1}H and ^{13}C NMR spectra, using different techniques (COSY, NOESY and HSQC), all protons were completely assigned (Fig. 4; see Section 3). The very well resolved seven-proton-pattern in the ^{1}H NMR spectra of the photoproducts **6a**,**b** between 2 and 6.5 ppm unmistakably pointed to the same benzobicyclo[3.2.1]octadiene structure. The multiplets in the lower field between 5 and 6.5 ppm are assigned to the **A** and **B** protons on the double bond whereas the **F** and **G** protons on methano bridge

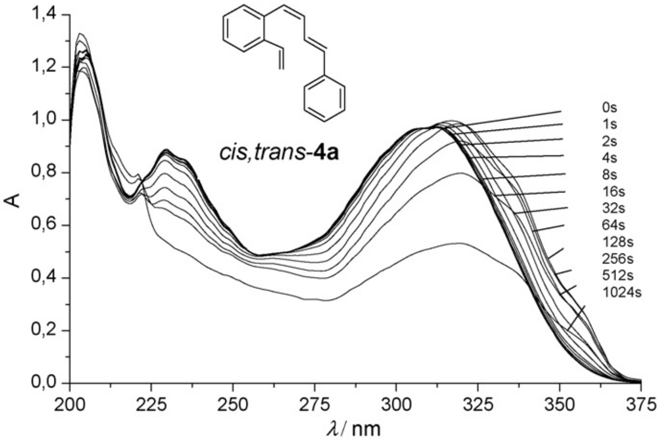

Fig. 3. The irradiation of *cis*,*trans*-**4a** followed by taking the UV spectra at indicated times.