

## Photochemistry of $\beta$ -(5-Substituted-2-furyl)-*o*-divinylbenzenes; Substituent Effects on the Reaction Course\*

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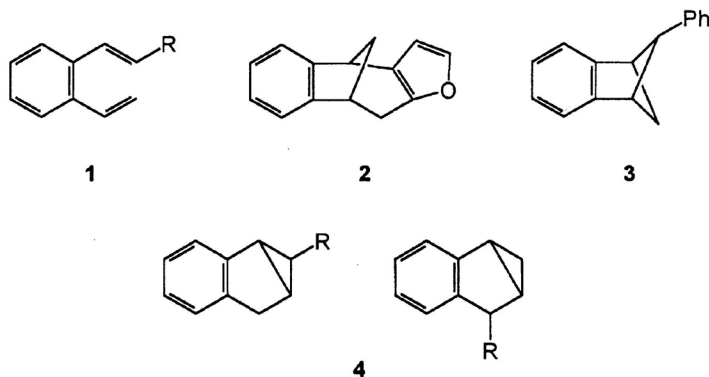
Irradiation of 2-[2-(2-vinylphenyl)ethenyl]furan (**1a**) and 5-methyl-2-[2-(2-vinylphenyl)ethenyl]furan (**1b**) gave 9,10-dihydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan (**2a**) and 9,10-dihydro-2-methyl-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan (**2b**), respectively, in a very good yield in addition to traces of **5**. Contrary to these results, the 5-substituted furan derivatives **1** (**c**: R = CN; **d**: R = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, **e**: R = OCH<sub>3</sub>) gave mainly, upon irradiation under the same conditions, isomerization about the double bond, high-molecular-weight products, small amount of phenanthrenes **5** and only traces of bicyclic structure **2**.

### INTRODUCTION

Intramolecular photochemical cycloadditions of *o*-divinylbenzene and its alkyl and/or aryl derivatives are well documented.<sup>1</sup> In one of our previous papers,<sup>2a</sup> in the series on the photochemistry of heteroaryl substituted *o*-divinylbenzenes (**1**),<sup>2</sup> we demonstrated the first example of the photochemical synthesis of [3.2.1] bicyclic compounds (**2**) by intramolecular cycloaddition of  $\beta$ -(2-furyl)-*o*-divinylbenzenes (**1**, R = 2-furyl).

\* Dedicated to the memory of Professor Stanko Borčić.

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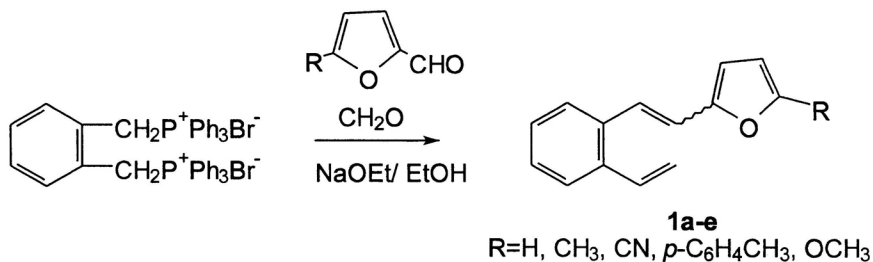


In comparison with the photochemical behaviour of  $\beta$ -aryl-*o*-divinylbenzenes (1, R = phenyl),<sup>3-6</sup> which undergo [2 + 2] cycloaddition and formation of the benzobicyclo[2.1.1]hexene derivative (3), and  $\beta$ -alkyl-*o*-divinylbenzenes (1, R = H, alkyl),<sup>7-8</sup> which undergo [4 + 2] cycloaddition giving benzobicyclo[3.1.0]hexene derivatives (4, R = H, alkyl),  $\beta$ -(2-furyl)-*o*-divinylbenzene (1, R = 2-furyl) is the sole system in which the  $\beta$ -substituent is involved in the intramolecular cycloaddition giving bicyclo[3.2.1]octadiene derivative (2) in a very good yield. Thus, it was of considerable interest from mechanistic and synthetic points of view, to study the photochemical behaviour of  $\beta$ -(2-furyl)-*o*-divinylbenzenes with different functionalities (1a-e) in order to obtain the bicyclic ring system as a versatile synthon for a variety of chemical transformations. This work reports the synthesis and photochemical reactions of 2-furyl derivatives substituted at position 5 of the furan ring.

## RESULTS AND DISCUSSION

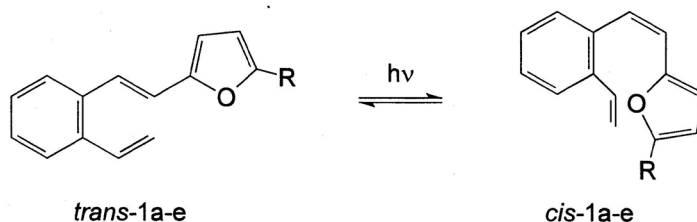
The starting compounds 1a-e were prepared *via* a known method,<sup>9,10</sup> using the Wittig reaction, from  $\alpha,\alpha'$ -*o*-xylyldi(triphenylphosphonium bromide) and the corresponding aldehydes (Scheme 1). They were obtained in good yield (35-80%) as mixtures of *trans*- and *cis*-isomers which were separated by column chromatography and identified spectroscopically.

Irradiation experiments were performed under anaerobic conditions. After initial *cis-trans* and/or *trans-cis* isomerization about the central double bond of 1a-e (Scheme 2), various photoproducts were isolated: bicyclo [3.2.1]octadiene derivatives 2, phenanthrenes 5 substituted at position 3 and the electrocyclicalisation products 6. Methoxy derivative 1e did not give any of these products, but yielded instead the isomers of 7, as a result of furan ring cleavage.



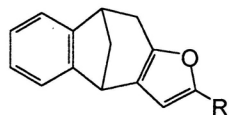
Scheme 1.

Identification of the products was mainly based on their <sup>1</sup>H-NMR data. NMR spectroscopy is very suitable for distinguishing between isomeric bicyclo[3.2.1]octadienes **2**, bicyclo[2.1.1]hexenes **3** and bicyclo[3.1.0]hexenes **4**. The obtained characteristic six proton-pattern in the <sup>1</sup>H-NMR spectra of photoproducts **2** between  $\delta = 2$  and 4 ppm, which was almost identical regardless of different substituents at position 5 of the furan ring, unmistakably pointed to the same type of photocycloaddition products. <sup>13</sup>C-NMR spectra, showing two doublets at 39 and 40 ppm and two triplets at 31 and 43 ppm, definitely confirmed the bicyclic [3.2.1] structure **2**, eliminating the presence of other possible structures such as **3** and/or **4**. The structures of phenanthrene derivatives **5b-d** and naphthofurans **6c-d** were based on <sup>1</sup>H-NMR spectra. The structure of phenanthrenes **5b** and **5d** were also confirmed by comparison with original samples unambiguously prepared by a sequence of reactions.<sup>11,12</sup>

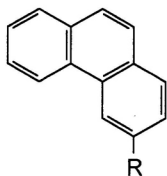


Scheme 2.

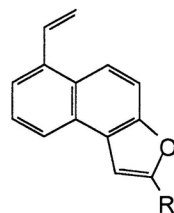
Irradiation of unsubstituted furan derivative **1a** and methyl substituted **1b** gave bicyclo[3.2.1]octadiene derivatives **2a** and **2b** in a more than 90% yield. Contrary to these results, the irradiation of **1c-e** gave, after a shorter time, only isomerization around the double bond and after prolonged irradiation a much high-molecular-weight material. However, by separation on



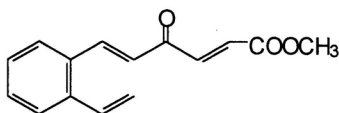
2a: R=H (90%)  
 2b: R=CH<sub>3</sub> (90%)  
 2c: R=CN (traces)  
 2d: R=*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (traces)



5b: R=CH<sub>3</sub>  
 5c: R=CN  
 5d: R=*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>



6c: R=CN  
 6d: R=*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>

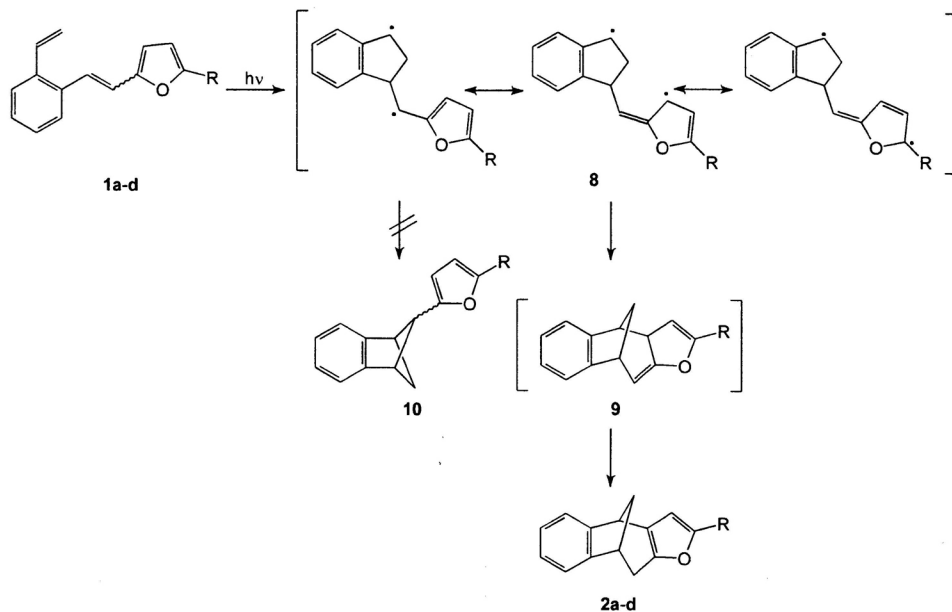


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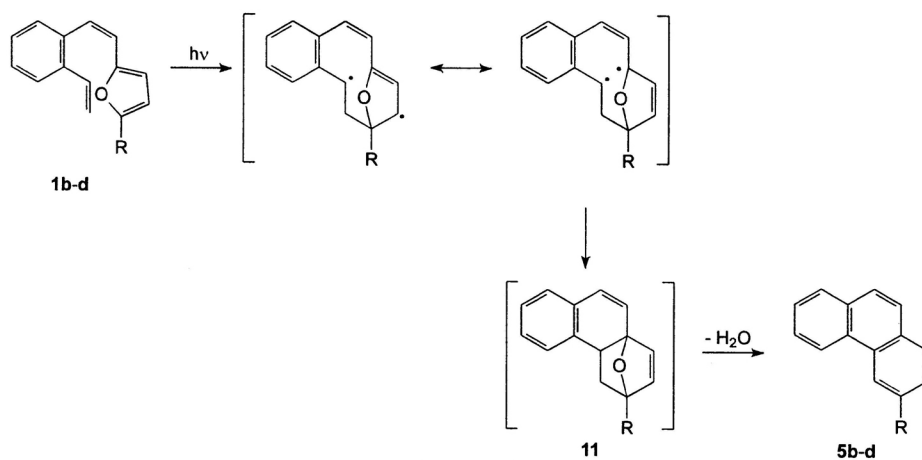
column chromatography, 2–3% of unexpected phenanthrenes **5c-d** were found and only traces of bicyclic structures **2c-d**. Phenanthrene **5b** was also formed upon irradiation of **1b**, as a side product in a 2% yield. It is obvious that substitution in the furan ring at position 5, either with an electron withdrawing (**1c**, R = CN) or electron donating (**1e**, R = OMe) group or with a group extending  $\pi$  delocalization (**1d**, R = Ph) substantially changed the reaction course in the excited state.

Formation of the photoproducts **2** and **5** may proceed *via* two different plausible pathways. The bicyclo[3.2.1]octadienes **2** can be explained (Scheme 3) from the singlet state of **1** by formation of 1,4-biradical<sup>6</sup> **8** followed by the preferred cyclohexene ring closure to **9**. By a photochemically allowed suprafacial 1,3-H shift, **9** is transformed into **2**. The cyclobutane ring closure to the bicyclo[2.1.1]hexene derivative **10** is a less favorable process. An explanation for the lack of reactivity of substituted derivatives **1c-e** could be the rate of intersystem crossing to the triplet state due to substituents.

The most likely way of the formation of phenanthrenes **5** is outlined in Scheme 4. We assume that from the *cis* configuration and suitable conformation of the starting compound **1** the initial photoinduced 1,4-biradical formation is followed by ring closure to the epoxy derivative **11**, which loses water during the work-up procedure and aromatizes to product **5**. This mechanism is supported by the correct position of the substituent in all obtained phenanthrenes. Formation of phenanthrenes **5** by thermal intramolecular Diels-Alder reaction of the vinyl group and the furan moiety of



Scheme 3.



Scheme 4.

the *cis*-1 is ruled out. Namely, no products were obtained in a tube that was kept in the dark during irradiation experiments.

Based on the results obtained thus far, we can conclude that for the synthetic application of photochemical ring closure to bicyclo[3.2.1]octadiene derivatives **2**, unsubstituted and methyl substituted **1** are the most useful starting materials.

## EXPERIMENTAL

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a JEOL FX-90 Q or a Varian GEMINI 300 instrument using  $\text{SiMe}_4$  as internal standard in  $\text{CDCl}_3$  solution. The electron impact mass spectra were recorded on an Extrel FT MS 2001. UV spectra were recorded on a Hitachi Perkin-Elmer 124 spectrometer. Silica gel (Merck 0.05–0.2 mm) was used for chromatographic purification. Irradiations were performed in a Quartz or Pyrex vessel in petroleum ether or benzene solutions and in the Rayonet reactor equipped with RPR 3000 A lamps. All irradiation experiments were carried out in degassed solutions by bubbling a stream of nitrogen prior to irradiation. Solvents were purified by distillation. Melting points were determined on a Kofler micro hot-stage (Reichert, Wien) and are uncorrected.

*5-Substituted 2-Furancarboxaldehydes*

2-Furancarboxaldehyde and 5-methyl-2-furancarboxaldehyde were commercially available. 5-Methoxy-2-furancarboxaldehyde<sup>13</sup> was prepared by bromination of 2-furancarboxaldehyde<sup>14</sup> followed by reaction with potassium methoxyde. 5-Cyano-2-furancarboxaldehyde<sup>15</sup> was prepared from 5-iodo-2-furancarboxaldehyde,<sup>16</sup> obtained from 5-bromo-2-furancarboxaldehyde.<sup>14</sup> 5-*p*-Tolyl-2-furancarboxaldehyde was prepared according to the described procedure.<sup>17, 18</sup>

*5-R-2-[2-(2-vinylphenyl)ethenyl]furans (1a-e)*

Starting compounds **1a** (R = H),<sup>9</sup> **1b** (R =  $\text{CH}_3$ ),<sup>9</sup> **1c** (R = CN), **1d** (R = *p*- $\text{C}_6\text{H}_4\text{CH}_3$ ),<sup>9</sup> **1e** (R =  $\text{OCH}_3$ ) were obtained by the method described<sup>9</sup> from equimolar quantities of  $\alpha, \alpha'$ -*o*-xylyl(ditriphenylphosphonium bromide) and the corresponding aldehydes in absolute ethanol and sodium ethoxyde as a base. The reaction mixture was purified and separated by repeated column chromatography on silica gel using petroleum ether as eluent. The first fractions yielded *cis*- and the last fractions *trans*-isomer. Characterizational data of new compounds (**1c,e**) are given below.

*5-Methoxy-2-[2-(2-vinylphenyl)ethenyl]furan (1e)*: yield 55%; according to  $^1\text{H}$ -NMR a mixture of 40% *cis*- and 60% *trans*-isomer;

*cis-1e*: oil; UV (EtOH)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 228 (4.20), 245 (4.14), 302 (4.07);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.60–7.15 (m, 4H, H-Ar), 6.91 (dd, 1H,  $J_{\text{trans}} = 17.58$  Hz,  $J_{\text{cis}} = 10.84$  Hz,  $-\text{CH}=\text{CH}_2$ ), 6.31 (s, 2H,  $-\text{CH}=\text{CH}-$ ), 5.84 (d, 1H,  $J = 3.22$  Hz, H-3f), 5.65 (dd, 1H,  $J_{\text{gem}} = 1.47$  Hz,  $J_{\text{trans}} = 17.58$  Hz, =CHH), 5.20 (dd, 1H,  $J_{\text{gem}} = 1.47$  Hz,  $J_{\text{cis}} = 10.84$  Hz, =CHH), 5.00 (d, 1H,  $J = 3.22$  Hz, H-4f), 3.69 (s, 3H,  $-\text{OCH}_3$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 160.6 (s), 142.6 (s), 136.6 (s), 135.7 (s), 134.8 (d), 129.2 (d), 127.2 (d), 127.1 (d), 124.9 (d), 123.1 (d), 119.0 (d), 114.7 (t), 111.5 (d), 81.7 (d), 57.2 (s);

*trans-1e*: m.p. 43–45 °C; UV (EtOH)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 225 (4.18), 262 (4.14), 338 (4.47); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3120, 3000, 2930, 2825, 1620, 1580, 1025;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.53–6.95 (m, 6H, H-Ar,  $-\text{CH}=\text{CH}-$ ,  $-\text{CH}=\text{CH}_2$ ), 6.60 (d, 1H,  $J_{\text{trans}} = 16.11$  Hz,  $-\text{CH}-\text{CH}-$ ), 6.22 (d, 1H,  $J = 3.22$  Hz, H-3f), 5.61 (dd, 1H,  $J_{\text{gem}} = 1.47$  Hz,  $J_{\text{trans}} = 17.58$  Hz, =CHH), 5.33 (dd, 1H,  $J_{\text{gem}} = 1.47$  Hz,  $J_{\text{cis}} = 10.48$  Hz, =CHH), 5.20 (d,  $J = 3.22$  Hz, H-4f), 3.89 (s, 3H,  $-\text{OCH}_3$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 161.5 (s), 143.9 (s), 135.9 (s), 135.2 (s), 134.8 (d), 127.5 (d), 126.8 (d), 126.3 (d), 125.1 (d), 121.0 (d),

118.1 (d), 115.9 (t), 110.6 (d), 81.6 (d), 57.4 (s); MS:  $m/z$  226 (M<sup>+</sup>), 221, 194, 167, 166, 165, 153, 129, 128, 115, 91, 77, 60, 55.

Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> (M<sub>r</sub> = 226.27): C 79.62, H 6.24%; found C 79.52, H 6.34%.

5-cyano-2-[2-(2-vinylphenyl)ethenyl]furan (**1c**): yield 35%, according to <sup>1</sup>H-NMR a mixture of 10% *cis*- and 90% *trans*-isomer;

*cis*-**1c**: oil; UV (EtOH)  $\lambda_{\max}/\text{nm}$  (log  $\epsilon$ ): 230 (4.05), 292 (4.08); IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2930, 2860, 2230, 1630, 1500; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.59 (d, 1H,  $J = 7.62$  Hz, H-Ar), 7.22–7.37 (m, 3H, H-Ar), 6.88 (d,  $J = 3.76$  Hz, H-4f), 6.86 and 6.52 (2d, 2H,  $J_{\text{cis}} = 12.14$  Hz,  $-\text{CH}=\text{CH}-$ ), 6.81 (dd, 1H,  $J_{\text{trans}} = 17.57$  Hz,  $J_{\text{cis}} = 11.02$  Hz,  $-\text{CH}=\text{CH}_2$ ), 5.85 (d, 1H,  $J = 3.76$ , H-3f), 5.68 (dd, 1H,  $J_{\text{trans}} = 17.57$  Hz,  $J_{\text{gem}} = 1.03$  Hz,  $=\text{CHH}$ ), 5.26 (dd, 1H,  $J_{\text{cis}} = 11.02$  Hz,  $J_{\text{gem}} = 1.03$  Hz,  $=\text{CHH}$ ); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 156 (s), 135.81 (s), 134.95 (s), 134.24 (d), 132.78 (d), 128.60 (d), 128.44 (d), 127.85 (d), 125.63 (d), 124.16 (s), 123.36 (d), 118.63 (d), 116.02 (t), 111.73 (s), 110.01 (d);

*trans*-**1c**: m.p. 34–35 °C; UV (EtOH)  $\lambda_{\max}/\text{nm}$  (log  $\epsilon$ ): 257 (4.08), 328 (4.41); IR (Nujol)  $\nu_{\max}/\text{cm}^{-1}$ : 2220, 1650; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.15–7.56 (m, 5H, 4H-Ar,  $-\text{CH}=\text{CH}-$ ), 7.11 (d, 1H,  $J = 3.80$  Hz, H-4f), 7.10 (dd, 1H,  $J_{\text{trans}} = 17.29$  Hz,  $J_{\text{cis}} = 11.13$  Hz,  $-\text{CH}=\text{CH}_2$ ), 6.76 (d, 1H,  $J_{\text{trans}} = 16.31$  Hz,  $-\text{CH}=\text{CH}-$ ), 6.42 (d, 1H,  $J = 3.80$  Hz, H-3f), 5.65 (dd, 1H,  $J_{\text{gem}} = 1.46$  Hz,  $J_{\text{trans}} = 17.29$  Hz,  $=\text{CHH}$ ), 5.44 (dd, 1H,  $J_{\text{cis}} = 11.13$  Hz,  $J_{\text{gem}} = 1.46$  Hz,  $=\text{CHH}$ ); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 157.7 (s), 137.1 (s), 134.4 (d), 133.6 (s), 129.9 (d), 128.8 (d), 127.1 (d), 126.9 (d), 125.9 (d), 124.0 (s), 123.8 (d), 117.5 (t), 116.5 (d), 111.9 (s), 109.0 (d); MS:  $m/z$  221 (M<sup>+</sup>, 50%), 165 (44), 115 (100); HRMS: M<sup>+</sup> calcd. 221.083515, M<sup>+</sup> exp. 221.079152.

Anal. Calcd. for C<sub>15</sub>H<sub>11</sub>NO (M<sub>r</sub> = 221.084): C 81.42, H 5.01%; found C 81.22, H 4.88%.

### Irradiation of **1a-e**, the Typical Procedure

Furan derivatives **1a-e** (10<sup>-2</sup>–10<sup>-3</sup> M) were dissolved in distilled petroleum ether or benzene, flushed with nitrogen for 30 min, and irradiated in a Quartz tube using a Rayonet Reactor with 300 nm lamps. After 20–80 h, the solvent was evaporated and the residue separated by column chromatography. Some of the compounds were found in to small quantities to be analyzed completely.

### Irradiation Products

9,10-Dihydro-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (**2a**) and 9,10-dihydro-2-methyl-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (**2b**): data given in Ref. 2a;

9,10-Dihydro-2-cyano-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (**2c**): <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.1–7.35 (m, 4H, H<sub>Ar</sub>), 6.94 (s, 1H, H<sub>F</sub>), 3.87 (d, 1H,  $J = 4.3$  Hz, H<sub>A</sub>), 3.68 (dd, 1H,  $J = 5.0$ ,  $J = 4.8$  Hz, H<sub>B</sub>), 3.16 (dd, 1H,  $J = 17.5$ ,  $J = 5.0$  Hz, H<sub>C</sub>), 2.67 (d, 1H,  $J = 17.5$  Hz, H<sub>D</sub>), 2.51 (ddd, 1H,  $J = 4.8$ ,  $J = 4.3$ ,  $J = 10.7$  Hz, H<sub>E</sub>), 2.04 (d, 1H,  $J = 10.7$  Hz, H<sub>F</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$ : 4 characteristic carbons in high field at: 42.6, 39.8, 39.0 and 31.3 ppm;

9,10-Dihydro-2-p-tolyl-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (**2d**): <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : aromatic hydrogens covered under those of *trans*-**1d**, 6.46 (s, 1H, H<sub>F</sub>), 3.83 (d, 1H,  $J = 4.3$  Hz, H<sub>A</sub>), 3.64 (dt, 1H,  $J = 5.0$  and 4.8 Hz, H<sub>B</sub>), 3.20

(dd, 1H,  $J = 16.5$  and  $5.0$  Hz,  $H_C$ ), 2.68 (d, 1H,  $J = 16.5$  Hz,  $H_D$ ), 2.43 (ddd, 1H,  $J = 10.5$ , 4.8 and 4.3 Hz,  $H_E$ ), 2.09 (d, 1H,  $J = 10.5$  Hz,  $H_F$ ).

**3-Methylphenanthrene (5b)**: yield 2%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.63–8.73 (m, 1H), 8.48 (s, 1H), 7.3–7.8 (m, 7H); identical with the original compound.<sup>11</sup>

**3-Cyanophenanthrene (5c)**: yield 2%; from the  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of the enriched fraction, the characteristic signals are at  $\delta/\text{ppm}$ : 9.0 (s, 1H) and 8.63 (d,  $J = 7.92$ , 1H).

**3-(p-Tolyl)phenanthrene (5d)**: yield 3%; m.p. 61–63 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.87 (d, 1H), 7.30–7.99 (m, 11H), 2.45 (s, 3H); MS:  $m/z$  268 ( $M^+$ , 100 %); HRMS:  $M^+$  calcd. 268.12500,  $M^+$  exp. 268.197033; the compound is identical with the authentic sample **5d**, unambiguously prepared by a sequence of reactions.<sup>12</sup>

**2-Cyano-6-vinylnaphtho[2.1-b]furan (6c)**: m.p. 74–76 °C; IR (neat):  $\nu_{\text{max}}/\text{cm}^{-1}$  2220 (CN);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.0–8.25 (2d,  $2H_{\text{ar}}$ ), 7.93 (s, 1H, H-1), 7.6–7.75 (m, 3H,  $H_{\text{ar}}$ ), 7.48 (dd, 1H,  $J_{\text{trans}} = 17.2$ ,  $J_{\text{cis}} = 10.95$  Hz,  $-\text{CH}=\text{CH}_2$ ), 5.82 (dd, 1H,  $J_{\text{trans}} = 17.2$ ,  $J_{\text{gem}} = 1.38$  Hz,  $=\text{CHH}$ ), 5.56 (dd, 1H,  $J_{\text{cis}} = 10.95$ ,  $J_{\text{gem}} = 1.38$  Hz,  $=\text{CHH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 154.24 (s), 137.33 (s), 134.52 (d), 128.34 (s), 127.83 (d), 127.76 (s), 126.77 (s), 126.06 (d), 124.19 (d), 123.21 (d), 121.98 (s), 118.71 (d), 117.65 (t), 112.15 (d); MS:  $m/z$  219 ( $M^+$ , 57 %), 193 (100); HRMS:  $M^+$  calcd. 219.067865,  $M^+$  exp. 219.064484.

**2-(p-Tolyl)-6-vinylbenzo[2,1-b]furan (6d)**:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : aromatic hydrogens covered under those of **5d**; 5.81 (dd, 1H,  $J_{\text{trans}} = 17.33$  Hz,  $J_{\text{gem}} = 1.43$  Hz,  $\text{CH}=\text{CHH}$ ), 5.51 (dd, 1H,  $J_{\text{cis}} = 10.90$  Hz,  $J_{\text{gem}} = 1.43$  Hz,  $\text{CH}=\text{CHH}$ ), 2.42 (s, 3H).

**Methyl-4-oxo-6-(2-vinylphenyl)hexa-2,5-dienoates (7)**: IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1725, 1658, 1600;

**cis-cis-7**: yield 6%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.0–7.6 (m, 5H,  $4H_{\text{ar}}$  and  $-\text{CH}=\text{CH}-\text{CO}-$ ), 6.77 (dd, 1H,  $J_{\text{trans}} = 17.3$ ,  $J_{\text{cis}} = 10.8$  Hz,  $-\text{CH}=\text{CH}_2$ ), 6.38 (d, 1H,  $J_{\text{cis}} = 12.0$  Hz,  $-\text{CH}=\text{CH}-\text{CO}-$ ), 6.04 and 5.56 ( $\text{AB}_q$ , 2H,  $J = 12.0$  Hz,  $-\text{CO}-\text{CH}=\text{CH}-\text{COOMe}$ ), 5.66 (dd, 1H,  $J_{\text{trans}} = 17.3$ ,  $J_{\text{gem}} = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ), 5.33 (dd, 1H,  $J_{\text{cis}} = 10.8$ ,  $J = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ).

**trans-cis-7**: yield 6%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.87 (d, 1H,  $J_{\text{trans}} = 16.4$  Hz,  $-\text{CH}=\text{CH}-\text{CO}-$ ), 7.15–7.65 (m,  $4H_{\text{ar}}$ ), 7.00 (dd, 1H,  $J_{\text{trans}} = 16.7$ ,  $J_{\text{cis}} = 10.8$  Hz,  $-\text{CH}=\text{CH}_2$ ), 6.74 (d, 1H,  $J_{\text{trans}} = 16.4$  Hz,  $-\text{CH}=\text{CH}-\text{CO}-$ ), 6.71 and 6.22 ( $\text{AB}_q$ , 2H,  $J_{\text{cis}} = 12.0$  Hz,  $-\text{CO}-\text{CH}=\text{CH}-\text{COOMe}$ ), 5.60 (dd, 1H,  $J_{\text{trans}} = 16.7$ ,  $J_{\text{gem}} = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ), 5.43 (dd, 1H,  $J_{\text{cis}} = 10.8$ ,  $J_{\text{gem}} = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ).

**trans-trans-7**: yield 5%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 8.08 (d, 1H,  $J_{\text{trans}} = 15.8$  Hz,  $-\text{CH}=\text{CH}-\text{CO}-$ ), 7.20–7.70 (m, 5H,  $4H_{\text{ar}}$  and  $-\text{CH}=\text{CH}-\text{CO}-$ ), 7.08 (dd, 1H,  $J_{\text{trans}} = 17.3$ ,  $J_{\text{cis}} = 10.8$  Hz,  $-\text{CH}=\text{CH}_2$ ), 6.88 (d, 1H,  $J_{\text{trans}} = 15.8$  Hz,  $-\text{CH}=\text{CH}-\text{COOMe}$ ), 6.82 (d, 1H,  $J_{\text{trans}} = 15.8$  Hz,  $-\text{CH}=\text{CH}-\text{CO}-$ ), 5.65 (dd, 1H,  $J_{\text{trans}} = 17.3$ ,  $J_{\text{gem}} = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ), 5.46 (dd, 1H,  $J_{\text{cis}} = 10.8$ ,  $J_{\text{gem}} = 1.2$  Hz,  $-\text{CH}=\text{CHH}$ ); MS:  $m/z$  242 ( $M^+$ , 2%), 183 (35), 129 (100), 128 (86).

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## REFERENCES

1. For review see W. H. Laarhoven, *Organic Photochemistry* **10** (1989) 163.
2. a) M. Šindler-Kulyk, L. Špoljarić, and Ž. Marinić, *Heterocycles* **29** (1989) 679;  
b) M. Šindler-Kulyk, S. Tomić, Ž. Marinić, and B. Metelko, *Recl. Trav. Chim. Pays-Bas* **114** (1995) 476.
3. M. Šindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.* **98** (1976) 1052; *ibid.* **100** (1978) 3816; *Recl. Trav. Chim. Pays-Bas*, **98** (1979) 187; *ibid.* **98** (1979) 452.
4. P. M. op den Brouw and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2* (1983) 1015; *ibid.* (1982) 795; *Recl. Trav. Chim. Pays-Bas* **101** (1982) 58; *J. Org. Chem.* **47** (1982) 1546.
5. P. M. op den Brouw, P. de Zeeuw, and W. H. Laarhoven, *J. Photochem.* **27** (1984) 327.
6. W. H. Laarhoven and Th. J. H. M. Cuppen, *J. Photochem.* **32** (1986) 105.
7. M. Pomerantz, *J. Am. Chem. Soc.* **89** (1967) 694; J. Meinwald and R. H. Mazzocchi, *ibid.* **89** (1967) 696.
8. J. Meinwald and D. Seeley, *Tetrahedron Lett.* (1970) 3739; L. Ulrich, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta* **53** (1970) 1323; H. Heimgartner, L. Ulrich, H. J. Hansen, and H. Schmid, *ibid.* **54** (1971) 2313.
9. M. Šindler-Kulyk, Z. Stiplošek, D. Vojnović, B. Metelko, and Ž. Marinić, *Heterocycles* **32** (1991) 2357.
10. M. Šindler-Kulyk, Z. Stiplošek, and B. Metelko, *Croat. Chem. Acta* **62** (1989) 81.
11. The authors thank Prof. W. Laarhoven for providing the sample.
12. 3-(*p*-tolyl)phenanthrene was prepared by the photochemical ring closure of *p*-tolylstilbene, obtained by the Wittig reaction from *p*-tolylbenzyl-triphenylphosphonium bromide and benzaldehyde in an overall yield of 15%.
13. V. N. Novikov and V. E. Polyakov, *Khim. Geterotsikl. Soed.* **6** (1982) 747.
14. Z. N. Nazarova, *Zh. Obsch. Khim.* **24** (1953) 575.
15. W. Hoyle and G. P. Roberts, *J. Med. Chem.* **16** (1973) 709.
16. Z. N. Nazarov a, *Zh. Obsch. Khim.* **25** (1955) 539.
17. L. Janda and Z. Voticky, *Chem. Zvesty* **38** (1984) 507.
18. R. Antonioletti, M. D'Auria, A. DeMico, G. Piancatelli, and A. Scettri, *J. Chem. Soc., Perkin Trans. 1* (1985) 1285.

## SAŽETAK

**Fotokemija  $\beta$ -(5-supstituiranih-2-furil)-*o*-divinilbenzena;  
utjecaj supstituenata na tijek reakcije**

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Osvjetljavanjem 2-[2-(2-vinilfenil)etenil]furana (**1a**) i 5-metil-2-[2-(2-vinilfenil)etenil]furana (**1b**) nastaje 9,10-dihidro-4,9-metano-4*H*-benzo[4,5]ciclohepta[1,2-*b*]furan (**2a**) odn. 9,10-dihidro-2-metil-4,9-metano-4*H*[4,5]ciclohepta[1,2-*b*]furan (**2b**) u vrlo dobrom iskorištenju, pored tragova spoja **5**. Nasuprot tome, osvjetljavanjem pod istim uvjetima 5-supstituiranih furanskih derivata **1** (**c**: R = CN; **d**: R = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, **e**: R = OCH<sub>3</sub>) zbiva se uglavnom izomerizacija oko dvostruke veze, tako da nastaju visokomolekularni produkti, mala količina fenantrena **5** i samo tragovi bicikličkog produkta **2**.