

OBSERVATION OF THE PRIMARY INTERMEDIATES IN THE  
PHOTOCHEMISTRY OF *o*-VINYLSTYRYLFURANS

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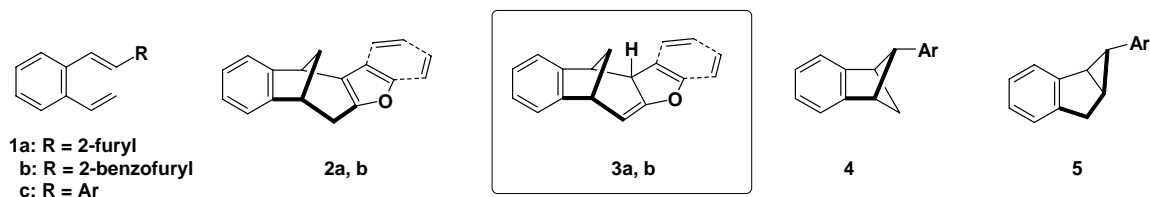
**Abstract** – The intermediates, 3a,9-dihydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan (**3a**) and 5b,11-dihydro-6,11-methano-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (**3b**), formed upon irradiation of 2-[2-(2-vinylphenyl)ethenyl]furan (**1a**) and 2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (**1b**), respectively, are determined and spectroscopically characterized. Whereas only the intermediate (**3b**) reacts photochemically with methanol to give the regioselective adduct (**6b**), both intermediates are trapped by molecular oxygen giving hydroproxides (**7a,b**), hydroxy- (**8a,b**) and keto derivatives (**9a, b**).

## INTRODUCTION

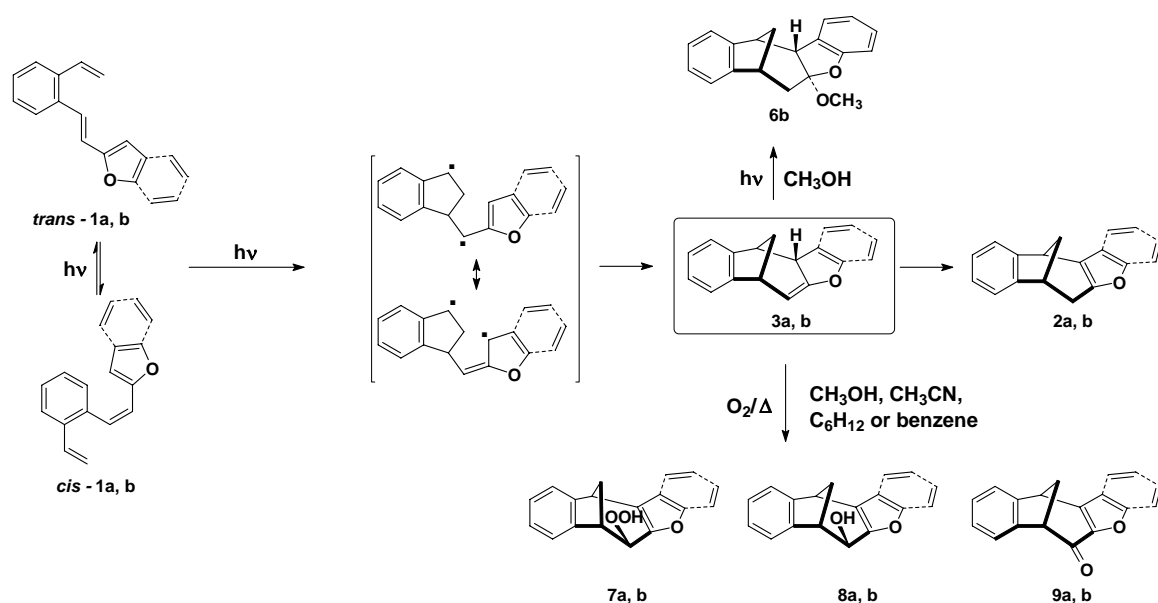
In one of our previous papers<sup>1a-c</sup> on the photochemistry of heteroaromatic stilbene like compounds<sup>1</sup> we demonstrated that upon irradiation of *o*-vinylstyrylfuran (**1a**) or –benzofuran (**1b**) benzobicyclo[3.2.1]octadiene derivative (**2a**) or (**2b**), respectively, is formed as the main photoproduct among some minor quantities of unidentified products and tarry material, when the irradiation was performed in diluted solutions. We have suggested that the products (**2a** and **b**) are formed *via* the corresponding intermediates (**3**) after 1,3-hydrogen shift. This was the first example of an intramolecular photocycloaddition with the participation of the heteroaromatic ring in contrast to the earlier results with the  $\beta$ -aryl substituted compound (**1c**),<sup>2</sup> where the main products are bicyclo[2.1.1]hexene derivatives (**4**) or bicyclo[3.1.0]hexene derivatives (**5**).

As an extension of our studies on photochemical reactions of heteroarylstilbene analogues<sup>1,3</sup> to polycyclic compounds with diverse functionality, we became interested in determining the previously proposed intermediate (**3**) as well as in identification of minor side-products, especially after observation that in

some experimental conditions they appear as dominant products.



## RESULTS AND DISCUSSION



Scheme1.

The starting compounds,<sup>1a, 1c</sup> 2-[2-(2-vinylphenyl)ethenyl]furan (**1a**) and 2-[2-(2-vinylphenyl)ethenyl]-benzo[*b*]furan (**1b**), prepared by the Wittig reaction according to the described procedure,<sup>3</sup> were usually irradiated in diluted benzene or petroleum ether solutions under anaerobic conditions for such a long time to ensure as good as possible conversion and formation of the bicyco[3.2.1]octadienes (**2a**, **2b**) (Scheme 1). The presence of the intermediates (**3a** or **b**) in the crude reaction mixtures was not observed. When the irradiation of **1a**, **b** was performed in methanol, in case of **1b**, the methoxy derivative (**6b**) was isolated<sup>1c</sup> as the main product. The existence of the intermediate (**3b**) and its trapping by methanol was anticipated. To detect the presumed intermediate (**3b**) and characterise it spectroscopically the experiment was performed in NMR tube irradiating the starting compound (**1b**) at 350 nm in deuterated benzene and following the photochemical course of reaction by recording the <sup>1</sup>H NMR spectra. After 20–40 min almost complete conversion to intermediate (**3b**) was observed. It is interesting to note that only one isomer, *endo*-**3** is formed (Figure 1). This is most probably because the major product usually results from the transition state that maximizes the  $\pi$  overlap. The same pattern of **3a** was seen in traces in <sup>1</sup>H NMR spectra of the crude reaction mixture after irradiation of **1a**. The structures of the intermediates were established by <sup>1</sup>H and <sup>13</sup>C NMR spectra using carbon-hydrogen and hydrogen-hydrogen 2D correlation

spectra.<sup>4</sup> NOE interaction between H<sub>F</sub> and H<sub>B</sub> protons undoubtedly pointed to the *endo*-configuration of the intermediate, the isomer with hydrogen oriented toward the methylene bridge.

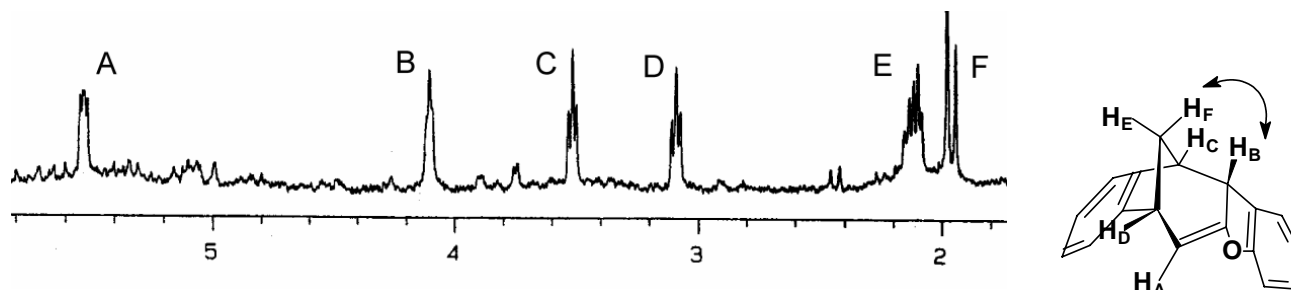
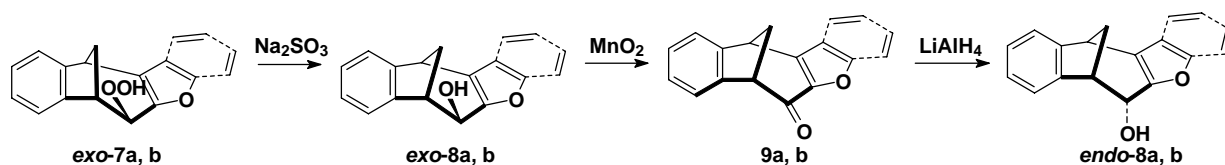


Figure 1. <sup>1</sup>H NMR spectrum of *endo*-**3b** (C<sub>6</sub>D<sub>6</sub>) and important NOE interaction

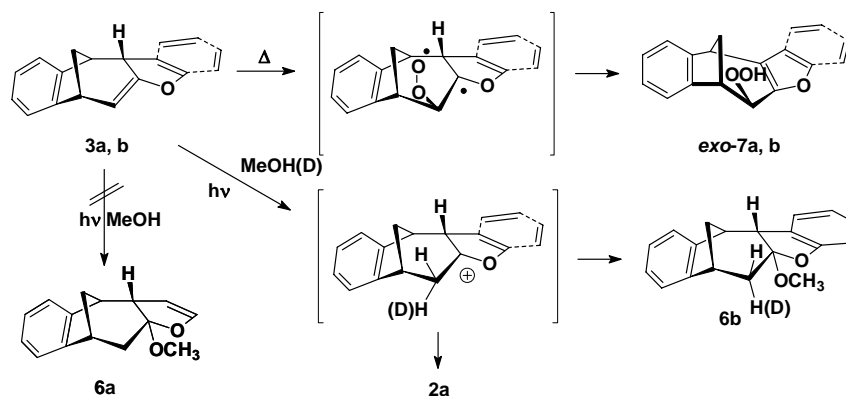
In some experiments, although performed under anaerobic conditions, the enhanced presence of minor side-oxygenation products was observed. To increase the yield of these minor products and to isolate them the experiment is done under aerobic conditions by bubbling air through the reaction mixture during the irradiation. After full conversion of the starting material (**1a**), only tarry material is detected. When the experiment is performed by bubbling the unpurified nitrogen direct from the cylinder the only product observed in <sup>1</sup>H NMR spectrum of the crude reaction mixture is the hydroperoxy *exo*-**7a** as a result of trapping of **3a** by oxygen. During the purification of the product by column chromatography some decomposition occurs so that the alcohol (*exo*-**8a**) and ketone (**9a**) are also isolated and their structures confirmed by converting one to an other derivative as shown in the Scheme 2. It should be emphasized that the *exo*-hydroxy derivative (*exo*-**8a**) formed from hydroperoxy (*exo*-**7a**) could be transformed *via* carbonyl derivative (**9a**) into its *endo*-isomer (*endo*-**8a**).



Scheme 2.

The same type of oxygenation products (**7b**, **8b**, **9b**) are noticed as side-products during the irradiation of **1b**. If the isolated intermediate (**3b**) is treated in dark in methanol at 45-50 °C for two days no addition of methanol takes place but the oxygenation products are the main products. This suggests that formation of the oxygenation products (**7 a,b**) is a result of the ground state oxygen addition<sup>5-7</sup> to the strained bridged double bond of the bicyco[3.2.1]octadiene intermediates (**2a**, **2b**) (Scheme 3). Further more, photochemical formation of the **7a** from **2a** could be ruled out due to non-absorption of **2a** at the irradiation conditions. However, it is evident that the mechanism of methanol addition<sup>1c</sup> and formation of **6b** requires the excited state (**3b**). This is confirmed by the irradiation of **1b** in deuteriomethanol<sup>1c</sup> in

which case the deuterio-**6b** was obtained. The protonation of the bridged double bond of the primary formed **3b** and formation<sup>8</sup> of the carbonium ion (Scheme 3) is assumed. The absence of **6a**/deutero-**6a** in the reaction mixture, when **1a** is irradiated in methanol/deuteriomethanol, might be explained by non-absorption of irradiation of the intermediate (**3a**) and the faster aromatisation process as a driving force for the formation of **2a**.



Scheme 3.

In summary, we have found a useful method for synthesizing new functionalised bridged polycyclic furan and benzofuran compounds by photochemical approach.

## EXPERIMENTAL

**General.** The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian GEMINI 300 and a Bruker AC 300 spectrometers at 300 and 75 MHz respectively in  $\text{CDCl}_3$  and where necessary in  $\text{C}_6\text{D}_6$ . The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on a Perkin Elmer LAMBDA 20 Spectrophotometer. FT-IR spectra were recorded on a Nicolet Magna-IR 760. HRMS spectra were measured on a Extrel FT MS 2001 DD. Melting points were determined on a Kofler micro hot-stage (Reichert, Wien) and are uncorrected. 2-Furancarboxaldehyde and 2-benzo[*b*]furancarboxaldehyde were obtained from commercial source.

Notations of H atoms in NMR spectra for all compounds are as assigned in **3b** (Figure 1).

**2-[2-(2-Vinylphenyl)ethenyl]furan (**1a**)<sup>1a</sup>** and **2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (**1b**)<sup>1c</sup>** were prepared by the one-pot Wittig reaction<sup>3</sup> from  $\alpha, \alpha'$ -*o*-xylyl(ditriphenylphosphonium bromide), formaldehyde and 2-furancarboxaldehyde or 2-benzofurancarboxaldehyde, respectively.

**Irradiation of 2-[2-(2-vinylphenyl)ethenyl]furan (**1a**) in methanol** (or benzene, cyclohexane, acetonitrile): A solution of 100 mg (0.51 mmol) of **1a** in 100 mL was irradiated at 300 nm in a Rayonet for 4 h in Pyrex tube bubbling the nitrogen directly from the cylinder (not deoxygenated). The solvent was evaporated in vacuum and the residue was chromatographed on a silica gel column as well as on

TLC plates using petroleum ether-dichloromethane and dichloromethane as the eluent, respectively. The following compounds were isolated:

**9,10-Dihydro-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (2a):** 25 mg (25%); identical to previously prepared.<sup>1a</sup>

**9,10-Dihydro-4,9-methano-10-*exo*-hydroperoxy-4H-benzo[4,5]cyclohepta[1,2-b]furan (*exo*-7a):** 21 mg (18%); colorless oil; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3416 (OH); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.40 (br s, 1H, OH), 7.36 (m, 1H, H<sub>ar</sub>), 7.18 (d, 1H, *J* 1.8 Hz, H<sub>fur</sub>), 7.14-7.18 (m, 1H, H<sub>ar</sub>), 7.04-7.08 (m, 2H, H<sub>ar</sub>), 6.28 (d, 1H, *J* 1.8 Hz, H<sub>fur</sub>), 4.94 (d, 1H, *J*<sub>AD</sub> 2.2 Hz, H<sub>A</sub>), 3.91 (dd, 1H, *J*<sub>AD</sub> 2.2, *J*<sub>DE</sub> 4.6 Hz, H<sub>D</sub>), 3.87 (d, 1H, *J*<sub>CE</sub> 4.0 Hz, H<sub>C</sub>), 2.41 (d, 1H, *J*<sub>EF</sub> 10.8 Hz, H<sub>F</sub>), 2.34 (ddd, 1H, *J*<sub>ED</sub> 4.6, *J*<sub>EC</sub> 4.0, *J*<sub>EF</sub> 10.8 Hz, H<sub>E</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  152.80 (s), 142.66 (s), 142.63 (d, C-H<sub>fur</sub>), 141.61 (s), 131.67 (s), 126.77 (d), 126.18 (d), 125.09 (d), 121.56 (d), 108.25 (d, C-H<sub>fur</sub>), 80.87 (d, C-H<sub>A</sub>), 44.41 (d, C-H<sub>D</sub>), 40.24 (t, C-H<sub>D</sub>, H<sub>E</sub>), 39.85 (d, C-H<sub>C</sub>); MS *m/z*: 228 (6, M<sup>+</sup>), 210 (100, M<sup>+</sup>-H<sub>2</sub>O), 181 (20), 153 (50); HRMS calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> 228.0781, found 228.0771.

**9,10-Dihydro-4,9-methano-10-*exo*-hydroxy-4H-benzo[4,5]cyclohepta[1,2-b]furan (*exo*-8a):** 14 mg (13%); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.41 (m, 1H, H<sub>ar</sub>), 7.15 (d, 1H, *J* 1.7 Hz, H<sub>fur</sub>), 7.12-7.15 (m, 1H, H<sub>ar</sub>), 7.03-7.06 (m, 2H, H<sub>ar</sub>), 6.26 (d, 1H, *J* 1.7 Hz, H<sub>fur</sub>), 4.65 (m, 1H, H<sub>A</sub>), 3.85 (dd, 1H, *J* 2.2, *J* 2.6 Hz, H<sub>C</sub>), 3.56 (m, 1H, H<sub>D</sub>), 2.36 (m, 2H, H<sub>E</sub>, H<sub>F</sub>), 2.21 (br s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  152.49 (s), 146.76 (s), 142.05 (s), 141.54 (d, C-H<sub>fur</sub>), 128.81 (s), 126.57 (d), 125.98 (d), 124.87 (d), 121.37 (d), 108.00 (d, C-H<sub>fur</sub>), 67.76 (d, C-H<sub>A</sub>), 48.96 (d, C-H<sub>D</sub>), 39.86 (t, C-H<sub>E</sub>, H<sub>F</sub>), 39.67 (d, C-H<sub>C</sub>); MS *m/z*: 212 (100, M<sup>+</sup>), 195 (52, M<sup>+</sup>-OH), 165 (61); HRMS calcd for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub> 212.0832, found 212.0854.

**9,10-Dihydro-4,9-methano-10-oxo-4H-benzo[4,5]cyclohepta[1,2-b]furan (9a):** 5 mg (4.6%); yellow crystals, mp 121 °C (hexane); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1673 (CO); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.42 (m, 1H, H<sub>ar</sub>), 7.36 (d, 1H, *J* 1.6 Hz, H<sub>fur</sub>), 7.28 (m, 1H, H<sub>ar</sub>), 7.06-7.09 (m, 2H, H<sub>ar</sub>), 6.48 (d, 1H, *J* 1.6 Hz, H<sub>fur</sub>), 4.20 (dd, 1H, *J* 1.8, *J* 2.2 Hz, H<sub>C</sub>), 4.00 (dd, 1H, *J* 1.7, *J* 2.8 Hz, H<sub>D</sub>), 2.82 (m, 2H, H<sub>E</sub>, H<sub>F</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  186.17 (s, C=O), 148.90 (s), 146.32 (d, C-H<sub>fur</sub>), 145.43 (s), 141.42 (s), 127.19 (d), 126.72 (d), 125.60 (d), 123.02 (d), 109.20 (d, C-H<sub>fur</sub>), 57.70 (d, C-H<sub>D</sub>), 52.73 (t, C-H<sub>E</sub>, H<sub>F</sub>), 42.10 (d, C-H<sub>C</sub>); MS *m/z*: 210 (100, M<sup>+</sup>), 181 (28), 153 (56); HRMS calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub> 210.0675, found 210.0657; Anal. Calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>: C, 79.98; H, 4.79. Found: C, 80.01; H, 4.96.

Only in the <sup>1</sup>H NMR spectrum of the crude reaction mixture the signals of the intermediate **3a** were present (**3a** disappears at purification on silica gel or aluminum oxide): **3a,9-dihydro-4,9-methano-4H-benzo[4,5]cyclohepta[1,2-b]furan (3a):** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.00-7.50 (m, 5H, 4H<sub>ar</sub>, H<sub>fur</sub>), 6.26 (t, 1H, *J*

2.8 Hz, H<sub>fur</sub>), 5.39 (dd, 1H, *J* 3.8, *J* 5.5 Hz, H<sub>A</sub>), 4.14 (m, 1H, H<sub>B</sub>), 3.76 (t, 1H, *J* 4.7 Hz, H<sub>C</sub>), 3.38 (dd, 1H, *J* 4.1, *J* 5.5 Hz, H<sub>D</sub>), 2.39 (ddd, 1H, *J* 4.1, *J* 4.7, *J* 10.7 Hz, H<sub>E</sub>), 2.26 (d, 1H, *J* 10.7 Hz, H<sub>F</sub>).

**Irradiation of 2-[2-(2-vinylphenyl)ethenyl]benzo[*b*]furan (1b)** in acetonitrile (or in benzene): Acetonitrile (or benzene) solution of 20 mg (0.08 mmol) of **1b** in 17 mL was purged with argon for 15 min and irradiated in a Rayonet at 350 nm for 70 min. The solvent was evaporated and the residue characterised spectroscopically without further purification.

**5b,11-Dihydro-6,11-methano-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (3b)**: colorless oil; UV(EtOH)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 248 (3.73), 258 (3.72), 275 (3.61), 287 (3.47), 310 (3.22); <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.74-7.10 (m, 7H), 6.55-6.61 (m, 1H, H<sub>I</sub>), 5.52 (dd, 1H, *J*<sub>AB</sub> 4.5 Hz, *J*<sub>AD</sub> 4.8 Hz, H<sub>A</sub>), 4.10 (dd, 1H, *J*<sub>AB</sub> 4.5 Hz, *J*<sub>BC</sub> 4.8 Hz, H<sub>B</sub>), 3.52 (dd, 1H, *J*<sub>BC</sub> 4.8 Hz, *J*<sub>CE</sub> 5.1 Hz, H<sub>C</sub>), 3.09 (dd, 1H, *J*<sub>AD</sub> 4.8 Hz, *J*<sub>ED</sub> 5.4 Hz, H<sub>D</sub>), 2.12 (ddd, 1H, *J*<sub>CE</sub> 5.1 Hz, *J*<sub>DE</sub> 5.4 Hz, *J*<sub>EF</sub> 10.8 Hz, H<sub>E</sub>), 1.96 (d, 1H, *J*<sub>EF</sub> 10.8 Hz, H<sub>F</sub>); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  159.34 (s), 154.54 (s), 154.38 (s), 140.55 (s) ~130 (s, covered by solvent), 127.26 (d), 127.11 (d), 126.74 (d), 126.45 (d), 123.47 (d), 121.98 (d), 120.80 (d), 110.47 (d, C-H<sub>ar</sub> close to oxygen), 107.40 (d, C-H<sub>A</sub>), 47.16 (d, C-H<sub>B</sub>), 44.50 (t, C-H<sub>E</sub>, H<sub>F</sub>), 42.87 (d, C-H<sub>C</sub>), 40.39 (d, C-H<sub>D</sub>).

#### Stirring of 3b in methanol.

The obtained **3b**, dissolved in 30 mL of methanol, was stirred at 45-50 °C for 2 h and then 2 days at rt. The solvent was removed in vacuum and the residue chromatographed using silica gel TLC plates and petroleum ether-ether(30%) as eluent. The following compounds were isolated.

**11,12-Dihydro-6,11-methano-12-*exo*-hydroperoxy-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (*exo*-7b)**: colorless oil; <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.48 (br s, 1H, OH), 7.43 (d, 1H, *J* 7.8 Hz), 7.20 (d, 1H, *J* 8.4 Hz), 6.96-7.12 (m, 4H), 6.80-6.92 (m, 2H), 4.99 (d, 1H, *J* 2.4 Hz, H<sub>A</sub>), 3.90 (dd, 1H, *J*<sub>DE</sub> 4.5 Hz, *J*<sub>AB</sub> 2.4 Hz, H<sub>D</sub>), 3.75 (d, 1H, *J*<sub>CE</sub> 4.8 Hz, H<sub>C</sub>), 2.43 (d, 1H, *J*<sub>EF</sub> 10.8 Hz, H<sub>F</sub>), 2.14 (ddd, 1H, *J*<sub>EF</sub> 10.8 Hz, *J*<sub>CE</sub> 4.8 Hz, *J*<sub>DE</sub> 4.5 Hz, H<sub>E</sub>); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  155.63 (s), 153.13 (s), 146.21 (s), 142.46 (s), 127.45 (d), 127.29 (2s), 126.98 (d), 125.71 (d), 125.42 (d), 123.23 (d), 122.05 (d), 119.64 (d), 112.48 (d), 81.70 (d, C-H<sub>A</sub>), 45.21 (d, C-H<sub>B</sub>), 40.48 (t, C-H<sub>E</sub>, H<sub>F</sub>), 38.62 (d, C-H<sub>C</sub>); MS (EI) *m/z*: 278 (M<sup>+</sup>, 15%), 262 (12), 245 (100), 202 (32), 115 (indenyl, 5).

**11,12-Dihydro-6,11-methano-12-oxo-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (9b)**: colorless oil; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1683 (C=O); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.80 (d, 1H, *J* 7.8 Hz), 7.44-7.52 (m, 3H), 7.31-7.39 (m, 2H), 7.07-7.13 (m, 2H), 4.55 (m, 1H), 4.17 (m, 1H), 2.99 (m, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  187.85 (s, C=O), 162.66 (s), 154.52 (s), 148.00 (s), 140.74 (s), 139.82 (s), 128.52 (d), 126.78 (d), 126.33 (d), 125.28 (d), 123.73 (s), 123.38 (d), 122.56 (d), 120.67 (d), 112.52 (d), 57.53 (d, C-H<sub>D</sub>), 52.19 (t, C-H<sub>E</sub>, H<sub>F</sub>), 39.97 (d, C-H<sub>C</sub>); MS *m/z*: 260 (M<sup>+</sup>, 100%), 202 (33); HRMS calcd for C<sub>18</sub>H<sub>12</sub>O<sub>2</sub> 260.0832, found 260.0773.

**11,12-Dihydro-6,11-methano-12-*exo*-hydroxy-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan** (*exo*-**8b**): colorless oil;  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  7.45 (d, 1H,  $J$  8.1 Hz), 7.23 (d, 1H,  $J$  8.1 Hz), 6.98-7.13 (m, 4H), 6.82-6.95 (m, 2H), 4.54 (m, 1H,  $\text{H}_\text{A}$ ), 3.74 (d, 1H,  $J_{\text{CE}}$  4.5 Hz,  $\text{H}_\text{C}$ ), 3.35 (m, 1H,  $\text{H}_\text{D}$ ), 2.25 (d, 1H,  $J_{\text{EF}}$  10.5 Hz,  $\text{H}_\text{F}$ ), 2.13 (ddd, 1H,  $J_{\text{EF}}$  10.5 Hz,  $J_{\text{ED}}$  4.8 Hz,  $J_{\text{EC}}$  4.5 Hz,  $\text{H}_\text{E}$ ), 1.70 (br s, 1H, OH);  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$ /ppm: 154.97 (s), 152.77 (s), 150.40 (s), 142.75 (s), 127.08 (d), 126.56 (d), 126.29 (s), 125.96 (s), 125.34 (d), 124.59 (d), 122.91 (d), 121.71 (d), 119.19 (d), 112.04 (d), 68.32 (d), 49.48 (d), 39.81 (t), 38.30 (d); MS (EI)  $m/z$ : 262 ( $\text{M}^+$ , 100%), 245 ( $\text{M}^+$ -OH, 67), 218 (78), 115 (indenyl, 25); HRMS calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_2$  262.0988, found 262.0967.

**Reduction of 7a and 7b:** Hydroperoxy **7a** or **7b** (0.04 mmol) was dissolved in 20 mL of dichloromethane and added to the 20 mL of saturated water solution of  $\text{Na}_2\text{SO}_3$ . Reaction mixture was stirred for 4 days. The organic layer was separated, water layer extracted with dichloromethane and combined dichloromethane solution dried over anhydrous  $\text{MgSO}_4$ . After evaporation of the solvent the  $^1\text{H-NMR}$  spectrum of the residue was identical to hydroxy **8a** or **8b**.

**Oxidation<sup>9</sup> of *exo*-8a and *exo*-8b:** In 40 mL of dichloromethane **8a** or **8b** (0.08 mmol) was dissolved, 200 mg (2.30 mmol) of  $\text{MnO}_2$  added. The mixture was stirred for 2 days at rt. The reaction mixture was filtered through silica gel column. The first fractions contained **9a** or **9b** (91%).

**Reduction<sup>10</sup> of 9a and 9b:** The ketone (**9a** or **9b**) (0.06 mmol) was dissolved in 15 mL of anhydrous ether and 10 mg of  $\text{LiAlH}_4$  (0.26 mmol) was added. The reaction mixture was stirred at rt for 2 days. Water was then added to destroy the excess lithium aluminum hydride. The ethereal solution was washed with 2 % hydrochloric acid and with water, and dried over anhydrous  $\text{MgSO}_4$ . The ether was evaporated in vacuum leaving ~ 80 % of *endo*-**8a** (*endo*-**8b**).

**9,10-Dihydro-4,9-methano-10-*endo*-hydroxy-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan** (*endo*-**8a**): colorless oil;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  6.95-7.30 (m, 4H,  $\text{H}_\text{ar}$ ), 6.93 (d, 1H,  $J$  1.5 Hz,  $\text{H}_\text{fur}$ ), 6.05 (d, 1H,  $J$  1.5 Hz,  $\text{H}_\text{fur}$ ), 4.97 (br s, 1H,  $\text{H}_\text{A}$ ), 3.47 (d, 1H,  $J$  4.2 Hz,  $\text{H}_\text{C}$ ), 3.38 (dd, 1H,  $J$  5.1,  $J$  5.7 Hz,  $\text{H}_\text{D}$ ), 2.20 (ddd, 1H,  $J_{\text{CE}}$  4.2,  $J_{\text{DE}}$  5.1 Hz,  $J_{\text{EF}}$  10.5 Hz,  $\text{H}_\text{E}$ ), 1.82 (d, 1H,  $J$  10.5 Hz,  $\text{H}_\text{F}$ ), OH signal covered. HRMS calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_2$  212.0832, found 212.0854.

**11,12-Dihydro-6,11-methano-12-*exo*-hydroxy-6*H*-benzo[4,5]cyclohepta[1,2-*b*]benzo[*d*]furan** (*endo*-**8b**):  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  7.44 (d, 1H,  $J$  7.5 Hz), 7.20-7.30 (m, 2H), 7.00-7.19 (m, 3H), 6.85-6.95 (m, 2H), 4.96 (m, 1H,  $\text{H}_\text{A}$ ), 3.67 (d, 1H,  $J_{\text{CE}}$  4.5 Hz,  $\text{H}_\text{C}$ ), 3.38 (dd, 1H,  $J_{\text{AB}}$  5.4,  $J_{\text{BE}}$  5.4 Hz,  $\text{H}_\text{B}$ ), 2.20 (ddd, 1H,  $J_{\text{EF}}$  10.5,  $J_{\text{BE}}$  5.4,  $J_{\text{CE}}$  4.5 Hz,  $\text{H}_\text{E}$ ), 1.77 (d, 1H,  $J_{\text{EF}}$  10.5 Hz,  $\text{H}_\text{F}$ ), 1.30 (br s, 1H, OH);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (singlets are not seen due to small quantity of the compound) 127.77 (d), 127.67 (d), 126.97 (d), 124.66 (d), 123.23 (d), 122.01 (d), 119.41 (d), 112.38 (d), 67.64 (d, C- $\text{H}_\text{A}$ ), 49.16 (d, C- $\text{H}_\text{B}$ ), 46.38 (t, C- $\text{H}_{\text{E,F}}$ ),

38.76 (d, C-H<sub>C</sub>); MS *m/z*: 262 (1.2, M<sup>+</sup>), 245 (100, M<sup>+</sup>-OH), 115 (15, indenyl); HRMS calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> 262.0988, found 262.0888.

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