Synthesis and Photochemistry of Styryl Substituted Annelated Furan Derivatives. IV. Concentration Directed Intra- and/or Intermolecular [2+2] Cycloaddition*,**

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New cyclobutane derivatives have been synthesized by intermolecular photochemical [2+2] ethene-ethene »head-to-head« (9a,b) and »head-to-tail« (10a,b–11a,b) as well as [2+2] ethene-furan (12a,b) cycloaddition from 2-[2-(2-vinylphenyl)ethenyl]benzo[b]furan (2a) and 2-[2-(2-methylphenyl)ethenyl]benzo[b]furan (2b), respectively. All compounds were isolated and characterized by spectroscopic methods. Under the benzene solution irradiation of 5 x 10⁻¹ mol dm⁻³ concentration and higher, 2-[2-(2-vinylphenyl)ethenyl]benzo[b]furan (2a) gave only dimeric products (9a–12a). At the 1 x 10⁻¹ mol dm⁻³ concentration, a mixture of dimers (9a–12a) and 7,12-dihydro-7,12-methano-6H-benzo[4,5]cyclohepta[1,2-b]benzofuran (5) was formed in a ratio 2:1.

Key words: synthesis, photochemistry, furan, cyclobutane, benzo[b]furan, cycloaddition

INTRODUCTION

Synthetic organic photochemistry, chemistry of the electronic excited states of a molecule, differs from the ground-state chemistry and provides a simple pathway to complicated structures, hard to obtain by a traditional synthetic approach.¹ Photochemical [2+2] cycloadditions²–³ belong to the best synthetic paths for the formation of cyclobutane and oxetane derivatives that may serve as intermediates for other compounds. From the viewpoint of mechanistic and preparative photochemistry, stilbenes⁴–⁵ showing very interesting photophysical and photochemical properties are among the most extensively investigated organic compounds. Our group is interested in heterocyclic analogs of o-vinylstilbenes and their photochemical intra- and molecular cycloaddition reactions.⁶

Photochemistry of styryl substituted annealed furan derivatives has been thoroughly investigated.⁷–¹² Upon irradiation in diluted petroleum ether or benzene solutions, furan (1) and benzo[b]furan (2a) derivatives of o-divinylbenzenes give benzobicyclo[3.2.1]octadiene derivatives 4 (Ref. 7) and 5,¹⁰ respectively, as the main photoproducts. No intramolecular cycloaddition product was found upon irradiation of naphthofuran derivative 3 (Ref. 10) under the same conditions in diluted solution. The only products observed were traces of dimeric cyclobutane derivatives. The intermolecular cycloaddition was attributed¹¹

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to fast excimer formation of 3. It is known that excimer formation is widespread among aromatic hydrocarbons and that this tendency increases with their size.\textsuperscript{13} [2,1-b]Naphthofuran derivative 3 in 10\textsuperscript{-3} mol dm\textsuperscript{-3} concentration undergoes intermolecular cycloadditions and formation of dimeric products 6–8 (Ref. 11) in a 60 % isolated yield. It was interesting to examine whether benzo- furan 2a and furan derivative 1 might also undergo similar conditions to give cyclobutanes. In this paper, the irradiation of furan derivative 1 and benzofuran derivative 2a in different solvent concentrations is described in order to study the concentration dependence on intra- versus intermolecular [2+2] cycloaddition and formation of benzbicyclo[3.2.1]octadiene and dimer structures, respectively.

RESULTS AND DISCUSSION

Benzene solutions of different concentrations of starting compounds 1 and 2a were irradiated under anaerobic conditions at 300 nm and in quartz tubes. Based on the \textsuperscript{1}H NMR spectra, the composition of the crude reaction mixture was established.

Upon irradiation of the 10\textsuperscript{-3}–10\textsuperscript{-2} mol dm\textsuperscript{-3} benzene solution, after complete conversion of the starting compounds 1 and 2a, the only products formed were bicyclo[3.2.1]octadiene derivatives 4 and 5, respectively, along with minor amounts of oxidation products,\textsuperscript{12} which also indicate the intramolecular cycloaddition process, but only as a result of incomplete anaerobic experimental conditions. At the concentration of 1 x 10\textsuperscript{-1} mol dm\textsuperscript{-3} and after complete conversion of the starting material 2a, a mixture of the dimeric products 9a–12a and bicyclo[3.2.1]octadiene structure 5 was found in a ratio 2:1. At the concentration of 5 x 10\textsuperscript{-1} mol dm\textsuperscript{-3}, only the dimeric products 9a–12a were detected. Under the same conditions, the furan derivative 1 gave no dimeric products (Scheme 1). After complete conversion of the starting material, only high-molecular-weight and decomposition products were found, besides bicyclo[3.2.1]octadiene structures.\textsuperscript{12}

The lack of reactivity of the furan derivative 1, furan analog of stilbene, towards [2+2]–dimerization might be explained by the faster polymerization and decomposition process and probably by the nonexistence of a complex in the excited state. Stilbenes\textsuperscript{2} and their derivatives form dimers similar to those (9–11) (Scheme 2) found on irradiation of benzofuran derivatives 2a and 2b.

The methyl substituted derivative 2b was irradiated as the model of an o-substituted conjugated system without a possibility of intramolecular cycloaddition and polymerization due to lack of the vinyl group. To isolate and characterize the new products (9–13) (Scheme 2), the methylstyryl benzofuran 2b and the vinylstyryl benzofuran 2a, respectively, were irradiated at one-molar concentrations. After 90 % conversion of the starting material 2b, a mixture of 81 % of dimers 9b–12b was isolated along with 7.6 % of high-molecular-weight products that remained on the column. Under the same conditions, the vinyl compound 2a also gave a mixture of dimers as the main product (48 %, 9a–12a) and more high-molecular-weight products (35 %) due to the parallel polymerization and decomposition process. In both cases, minor amounts of electrocyclization products 13a,b were identified. The photoproducts were isolated by column chromatography followed by repeated thin-layer chromatography and their structures were determined by spectroscopic methods.\textsuperscript{13,16} As regards the cis-trans isomerization of the starting compounds and the existence of both isomers in the photochemical mixture, one can expect eleven isomers to be formed by trans-trans, trans-cis and cis-cis dimerization in »head-to-head« and »head-to-tail« modes. Structure determination of the isolated isomers (9–11) as »head-to-head« (9) or »head-to-tail« (10–11) adducts was based on the MS spectra analysis. All dimers (9–11) showed the base peak at M+2 and only dimer 9 showed two fragments characteristic of an unsymmetrical reversion. The stereo orientation of the cyclobutane hydrogens was de-
terminated from their $^1$H NMR spectra (see Experimental) combined with the COSY and NOESY experiments, using a different mixing time. The fused cyclobutane structures 12a,b formed by [2+2] ethene-furan cycloaddition were deduced from the $^1$H NMR spectra and are in good agreement with the previously described structure. In summary, we can conclude that, regardless of concentration, styril naphthofuran 3 underwent intramolecular cycloaddition reactions depending on the concentration. For the synthesis of cyclobutane derivatives 9–12, without formation of bicyclo[3.2.1]octadiene compound 5, the best concentration of the starting compound 2a was higher than 5 x 10$^{-3}$ mol dm$^{-3}$.

**EXPERIMENTAL**

**General**

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian GEMINI 300 spectrometer at 300 and 75 MHz, respectively, in CDCl$_3$ and, where necessary, in C$_6$D$_6$ and Me$_4$Si as internal standards. The assignment of the signals was based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on a Perkin Elmer LAMBDA 20 Spectrophotometer. HRMS spectra were measured on an Auto Spec Q (VG Analytical Manchester, GB). Elemental analyses were carried out in the Microanalytical Laboratory of the Rugjer Bošković Institute. Irradiations were performed in a quartz or Pyrex vessel in benzene solutions and in the Rayonet reactor equipped with RPR 3000 Å lamps. Standard column chromatography was carried out on silica gel 60–230 mesh ASTM. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F$_{254}$ plates. All irradiation experiments were carried out in deaerated solutions by bubbling a stream of nitrogen or argon prior to irradiation. Solvents were purified by distillation. Melting points were determined on a Kofler micro hot-stage (Reichert, Wien) and are uncorrected.

2-[2-(2-Vinylphenyl)ethyl]furan (1)$^{17}$ and 2-[2-(2-vinylphenyl)ethyl]benzo[f]furan (2a)$^{10}$ were prepared by the Wittig one-pot reaction from $\alpha$-$\omega$-xylyl(ditriphenylphosphonium bromide), formaldehyde and the corresponding carboxaldehydes as described.

2-[2-(2-Methylphenyl)ethyl]benzo[h]furan (2b) was prepared from o-methylbenzyltriphenylphosphonium bromide (3.34 g, 7.0 mmol) and 2-formylbenzo[h]furan (1.02 g, 7.0 mmol) with sodium ethoxide as the base according to the described procedure$^{10,18}$ in 94 % yield (1.54 g; cis:trans = 37:63). The reaction mixture was purified and separated by repeated column chromatography on silica gel using a petroleum ether/diethyl ether mixture as eluent. The first fractions yielded a cis- and the last fractions a trans-isomer. Characterization data of the new compounds are given below:

**cis-2b**

Colorless oil; UV(ethanol) $\lambda_{\text{max/nm}}$ (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 307 (4.26), 299 (4.23, sh), 290 (4.11, sh); $^1$H NMR (CDCl$_3$) $\delta$/ppm: 7.40–7.34 (m, 2H), 7.32 (d, 1H, $J$ = 8.1 Hz), 7.27–7.14 (m, 4H), 7.11 (t, 1H, $J$ = 7.2 Hz), 6.74 (d, 1H, $J$ = 12.3 Hz), 6.59 (d, 1H, $J$ = 12.3 Hz), 6.25 (s, 1H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$/ppm: 154.08 (s), 153.99 (s), 136.75 (s), 135.94 (s), 131.34 (d), 130.00 (d), 128.71 (s), 128.65 (d), 128.60 (d), 124.31 (d), 122.66 (d), 120.79 (d), 119.24 (d), 110.92 (d), 105.29 (d), 19.57 (q).

**trans-2b**

Colorless crystals; m.p. 59–60 °C; UV(ethanol) $\lambda_{\text{max/nm}}$ (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 355 (4.23, sh), 338 (4.49), 325 (4.48), 230 (3.91), 208 (4.22); $^1$H NMR (CDCl$_3$) $\delta$/ppm: 7.55–7.43 (m, 4H), 7.41 (d, 1H, $J$ = 8.1 Hz), 7.23–7.12 (m, 5H), 6.84 (d, 1H, $J$ = 15.9 Hz), 6.59 (s, 1H), 2.41 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$/ppm: 155.31 (s), 154.90 (s), 136.27 (s), 135.47 (s), 130.58 (d), 129.11 (s), 128.02 (d), 127.78 (d), 126.20 (d), 125.05 (d), 124.56 (d), 122.83 (d), 120.77 (d), 117.40 (d), 110.85 (d), 105.12 (d), 19.76 (q); MS $m/z$: 234 (M$^+$, 63 %), 219 (35), 189 (25), 128 (100), 115 (22); HRMS: calcd. M$^+$ = 234.103916; found: M$^+$ = 234.106411.

Anal. Calcd. for C$_{22}$H$_{16}$O (M$_r$ = 234.29): C 87.15, H 6.02 %. found: C 87.01, H 6.03 %.

**Irradiation Experiments**

A benzene solution (0.9 mol dm$^{-3}$) of 2a (340 mg) and 2b (330 mg), respectively, was irradiated under argon for 50–60 h in Rayonet at 300 nm in a Pyrex tube. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column and TLC plates using petroleum ether/diethyl ether as eluent.

**Irradiation of 2-[2-(2-Vinylphenyl)ethyl]benzo[f]/furan (2)**

4-Vinylbenzo[d]naphth[2,1-b]furan (13a)$^{10}$ was eluted in the first fractions from the column in traces, followed by 12 % of 2a. By eluting with the more polar petroleum ether/diethyl ether (0–50 %) solution, a mixture of dimeric products 9a–12a (147 mg, 42.7 %) was separated along with some minor quantities of unidentified dimeric products (17 mg, 5 %). The tarry material (35.4 %) remained on the column.

Anal. Calcd. for the mixture of dimeric products C$_{36}$H$_{28}$O$_2$ (M$_r$ = 492.62): C 87.78; H 5.73 %. found: C 87.75; H 5.95 %.

After repeated chromatography on TLC using petroleum ether/diethyl ether (10–50 %) and petroleum ether/dichloromethane (20 %) as eluent from the mixture of dimeric products, the formed dimers 9a–12a were isolated one by one:
12 mg (3.5 %); yellow oil; UV(EtOH) $\lambda_{max}$/nm (log $\varepsilon$/d$^{-1}$ mol$^{-1}$ cm$^{-1}$): 248 (4.52), 278 (4.04), 286 (4.00); $^1$H NMR (C$_6$D$_6$) $\delta$/ppm: 7.65 (d, 2H, $J = 7.5$ Hz, 6'-H), 7.41 (m, 2H, 2H, H-7, H$_5$), 7.33–7.25 (m, 4H, H$_8$), 7.10–6.99 (m, 8H, H$_9$). 6.79 (dd, 2H, $J = 17.1, 10.8$ Hz, 3'''-H), 6.16 (s, 2H, 3'-H), 5.22 (dd, 2H, $J = 17.1, 1.5$ Hz, 1''-H), 4.47 (dd, 2H, $J = 10.8, 1.5$ Hz, 2''-H), 4.59 (dd, 2H, $J = 9.9$ Hz, 3',H-4), 4.17 (d, 2H, $J = 9.9$ Hz, 1-H,2-H); $^1$C NMR (C$_6$D$_6$) $\delta$/ppm: 157.92 (s), 156.03 (s), 153.50 (d, C-3'''), 127.74 (d), 127.35 (d), 127.26 (d), 127.15 (d), 124.59 (d), 124.35 (d), 121.45 (d), 116.59 (t, C-1''',2'''), 111.73 (d, C-7'), 104.50 (d, C-6'), 123.12 (d, C-5'), 121.13 (d, C-4'), 116.56 (t, C-1'-H), 47.25 (d), 44.73 (d); MS $m$/z: 492 (M$^+$, $^{1}H$), 260 (M$^+$–CH$_2$=CHCOCH$_3$, 100), 232 (CH$_2$=CHCOCH$_3$, 2H, C-3''').

3-Benzo-7-(2-benzofuryl)-6-(2-vinylphenyl)-1-[2-(2-vinylphenyl)ethenyl]-2-oxabicyclo[3.2.0]hept-3-ene (12a)

36 mg (10.6 %); colorless crystals; m.p. 148–149 °C; UV(NGOH) $\lambda_{max}$/nm (log $\varepsilon$/d$^{-1}$ mol$^{-1}$ cm$^{-1}$): 213 (4.54), 245 (4.41), 251 (4.42), 256 (4.39), 279 (3.96), 285 (3.92); $^1$H NMR (C$_6$D$_6$) $\delta$/ppm: 7.50 (d, 2H, $J = 7.5$ Hz, 6'-H), 7.24 (d, 2H, $J = 8.7$ Hz, 7'-H), 7.22 (d, 2H, $J = 7.5$ Hz, 3'''-H), 7.20 (d, 2H, $J = 7.5$ Hz, 4''-H), 7.03 (dd, 2H, $J = 16.8, 11.1$ Hz, 3''-H), 7.02 (t, 2H, $J = 7.5$ Hz, 5'''-H), 6.92 (t, 2H, $J = 7.5$ Hz, 6'''-H), 6.90 (t, 2H, $J = 7.5$ Hz, 4'''-H), 6.02 (s, 2H, 2'''-H), 3.28 (dd, 2H, $J = 16.8, 1.5$ Hz, 1''''-H), 5.11 (dd, 2H, $J = 11.1, 1.5$ Hz, 5''''-H), 4.89 (dd, 2H, $J = 7.7, 6.3$ Hz), 4.88 (dd, 2H, $J = 7.7, 6.3$ Hz); $^{13}$C NMR (C$_6$D$_6$) $\delta$/ppm: 158.00 (s), 155.39 (s), 138.41 (s), 136.72 (s), 135.49 (d, C-3'''), 128.30 (d, C-5'''), 127.65 (d, C-4'''), 126.78 (d, C-6'''), 126.63 (d, C-3'''), 124.23 (d, C-6'), 123.12 (d, C-5), 121.13 (d, C-4), 116.56 (t, C-1''''-2'''''), 110.33 (d, C-7), 104.76 (d, C-6'), 44.32 (d), 41.36 (d); MS (FAB) $m$/z: 492 (M$^+$, $^{1}H$), 246 (M$^+$, 36), 131 (benzofurylmethyl, 29).

56 mg (16.5 %); m.p. 58–59 °C; UV(EGOH) $\lambda_{max}$/nm (log $\varepsilon$/d$^{-1}$ mol$^{-1}$ cm$^{-1}$): 246 (4.56), 277 (4.04), 286 (4.02); $^1$H NMR (C$_6$D$_6$) $\delta$/ppm: 7.28–7.08 (m, 8H, H-7, H$_9$), 6.96–6.88 (m, 8H, H$_8$), 6.98 (dd, 2H, $J = 17.1, 10.8$ Hz, 3''-H), 6.32 (s, 2H, 3'-H), 5.33 (dd, 2H, $J = 17.1, 1.5$ Hz, 1''-H), 5.07 (dd, 2H, $J = 6.6$ Hz, 1-H,3-H), 4.47 (dd, 2H, $J = 6.6$ Hz, 2-H,3-H); $^{13}$C NMR (C$_6$D$_6$) $\delta$/ppm: 158.09 (s), 158.81 (s), 138.41 (s), 137.24 (s), 135.67 (d, C-3''''), 128.40 (d), 127.40 (d), 127.35 (d), 127.01 (d), 124.38 (d), 122.33 (d), 121.27 (d), 116.05 (t, C-1''''-2'''''), 111.49 (d, C-7), 104.51 (d, C-3'), 44.62 (d, C-1, 3.4, 42.07 (d, C-2, 4, 246 (M$^+$, 81), 131 (benzofurylmethyl, 100).

2,2'-{(r-1-t-c-2-t-3-t-4)-2,4-Bis(2-vinylphenyl)cyclobutane-1,3-diyl}[bis-1-benzofuran [r-tct hit dimer] (10a)

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(d), 121.37 (d), 116.54 (t, C-1',2',7'), 116.34 (t, C-1',2'), 111.72 (2d, C-5,C-4'), 105.01 (d, C-3), 91.56 (s, C-7a), 52.91 (d, C-5b), 48.99 (d, C-7), 40.86 (d, C-6); MS (EI) m/z: 492 (M+, <1 %), 246 (M+2/2, 48), 131 (benzofuranyl methyl, 100).

Irradiation of 2-[2-(2-Methylphenyl)ethenyl]benzo[b]-furan (2b)

4-Methylbenzo[d]naphth[2,1-b]furan (13b) was eluted (petroleum ether/dichloromethane 0–20 %) in the first fractions from the column in 1.2 % yield, followed by a mixture of cis- (1.8 %) and trans- (8.2 %) isomers of 2b. In the last fractions a mixture of dimeric products 9b–12b (225 mg, 68.2 %) was separated along with some minor quantities of unidentified dimeric products (43 mg, 13 %). The tarry material (7.6 %) remained on the column.

Anal. Calcd. for C17H12O (Mr = 232.28): C 87.90, H 5.21 %; found: C 87.72, H 5.29 %.

After repeated chromatography on TLC using petroleum ether/diethyl ether (5–15 %) and petroleum ether/dichloromethane (20–30 %) as eluents from the mixture of dimeric products, the formed dimers 9b–12b were isolated one by one:

4-Methylbenzo[d]naphth[2,1-b]furan (13b)

4 mg (1.2 %); colorless crystals; m.p. 146–147 °C; UV(EtOH) λmax/nm (log ε/dm3 mol−1 cm−1): 228 (4.36), 230 (4.36), 240 (4.55), 247 (4.59), 268 (3.56), 281 (3.34), 304 (3.98), 313 (4.17), 326 (4.00), 335 (3.88), 341 (4.13); 1H NMR (CDCl3) δ/ppm: 8.51 (1H, d, J = 8.1 Hz), 8.39 (1H, dd, J = 7.2, 1.8 Hz), 8.09 (1H, d, J = 9.0 Hz), 7.78 (1H, d, J = 9.0 Hz), 7.69 (1H, d, J = 7.2, 1.8 Hz), 7.60 (1H, d, J = 7.5 Hz), 7.54–7.42 (m, 2H), 7.38 (1H, d, J = 7.2 Hz), 2.79 (3H, s); 13C NMR (CDCl3) δ/ppm: 157.51 (s), 154.97 (s), 139.52 (s), 136.52 (s), 130.29 (d, C-3'), 126.68 (s, C-4'), 126.31 (d, C-5'), 126.17 (d, C-6'), 123.66 (d, C-6), 122.63 (d, C-5), 120.59 (d, C-4'), 111.04 (d, C-7), 103.33 (d, C-3'), 46.14 (d, C-6'), 43.84 (d, C-1'), 19.70 (q, CH3); MS m/z: 468 (M+, <1 %), 260 (M+ - CH3C6H4CH=CHC6H4CH2CH3, 10), 234 (M+2/2, 18), 207 (CH3C6H4CH=CHC6H4CH2, 7).

2,2'-[t-1c-2-t,3-t,4]-2,4-Bis(2-methylphenyl)cyclobutane-1,3-diy]bis-1-benzofuran [t -ctt htt dimer] (10b)


22 mg (6.7 %); colorless crystals; m.p. 53–54 °C; UV(EtOH) λmax/nm (log ε/dm3 mol−1 cm−1): 250 (4.46), 279 (4.11), 286 (4.11); 1H NMR (CDCl3) δ/ppm: 7.70 (2H, d, J = 7.2 Hz, 6'-H), 7.50 (d, 2H, J = 8.1 Hz, 7'-H), 7.45 (d, 2H, J = 7.5 Hz, 4'-H), 7.30 (t, 2H, J = 7.2 Hz, 5'-H), 7.25 (dd, 2H, J = 8.1, 7.5 Hz, 6'-H), 7.18 (t, 2H, J = 7.5 Hz, 5'-H), 7.13 (t, 2H, J = 7.2 Hz, 4'-H), 7.06 (2H, J = 7.2 Hz, 3'-H), 6.48 (2H, 3'-H), 4.32 (2H, J = 9.3 Hz, 3-H,4-H), 4.01 (d, 2H, J = 9.3 Hz, 1-H,2-H), 2.03 (s, 6H, CH3); 13C NMR (CDCl3) δ/ppm: 157.51 (s), 154.97 (s), 139.52 (s), 136.52 (s), 130.29 (d, C-3'), 126.68 (s, C-4'), 126.31 (d, C-5'), 126.17 (d, C-6'), 123.66 (d, C-6), 122.63 (d, C-5), 120.59 (d, C-4'), 111.04 (d, C-7), 103.33 (d, C-3'), 46.14 (d, C-6'), 43.84 (d, C-1'), 19.70 (q, CH3); MS m/z: 468 (M+, <1 %), 260 (M+ - CH3C6H4CH=CHC6H4CH2CH3, 10), 234 (M+2/2, 18), 207 (CH3C6H4CH=CHC6H4CH2, 7).

2,2'-[t-1c-2-t,3-t,4]-2,4-Bis(2-methylphenyl)cyclobutane-1,3-diy]bis-1-benzofuran [t -ctt htt dimer] (10b)
3-Benz-7-(2-benzofuryl)-6-(2-methylphenyl)-1-[(2-(2-methylphenylethenyl)-2-oxabicycle[3.2.0]hept-3-ene (12b)

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1. See Synthesis No. 8 (2001), Special topic issue in Organic Photochemistry (dedicated to Prof. H. E. Zimmerman).

SAŽETAK
Sinteza i fotokemija stiril-supstituiranih aneliranih furan-derivata.
IV. Koncentracijski usmjeravana intra- i/iili intermolekularna [2+2] cikloadicija
Irena Škorić, Željko Marinić i Marija Štindler-Kulyk

Sintetizirani su novi ciklobutanski derivati intermolekularnom fotokemijskom [2+2] eten-eten »glava-glava« (9a,b) i »glava-rep« (10a,b,11a,b) kao i [2+2] eten-furan (12a,b) cikloadicijom iz [2-(2-vinileniletetilen)]benzo[furanu (2a) odnosno 2-[(2-(2-metilfeniletetilen)]benzo[furanu (2b). Svi su spojevi izolirani i spektroskopski okarakterizirani. Kod osvjetljavanja benzenskih otopina koncentracije 5 × 10⁻¹ mol dm⁻³ i viših, 2-(2-(vinileniletetilen)iletetilen)benzo[furan (2a) daje samo dimerne produkte (9a–12a). Kod koncentracije 1 × 10⁻² mol dm⁻³ nastaje smjesa dimer (9a–12a) i 7,12-dihidro-7,12-metano-6H-benzo[4,5]ciklohepta[1,2-b]benzofuran (5) u omjeru 2:1.