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Structure elucidation of the photoproducts obtained by the photolysis of *N*-acetyl-2-styrylpyrroles

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Abstract

From the irradiation mixture of *N*-acetyl-2-styrylpyrroles (**5a**, **b**) the deacylated (**6a**, **b**), phototransposition (**7a**, **b**–**10a**, **b**), electrocyclisation (**12**), addition and reduction (**11**, **13** and **14**) and dimerisation products (**15**) have been detected. No intramolecular cycloaddition products have been observed.

Keywords: Pyrroles; Photochemistry; Phototransposition; Photolysis; Oxidation potentials; Electron transfer; Acetylation

1. Introduction

Since our first paper in 1989 [1] about the photochemistry of 2-styrylfuran (**1a**) and attempt to use photochemical approach to hetero-polycyclic compounds many modified heterocyclic compounds have been synthesized and their photochemical behaviour examined [2–13] (Scheme 1). It has been found that the β-furan derivative of *o*-divinylbenzene (**1a**) undergoes intramolecular [2 + 2] photocycloaddition giving bicyclo[3.2.1]octadiene structure (**2a**) [1]. Similar results have been obtained with 5-substituted furan derivatives [1,4] as well as with annelated benzofuran derivative [6]. Contrary to these, naphthofuran derivatives, due to fast complex formation in the excited state, give intermolecular [2 + 2] cycloaddition even at the 10^{-4} M concentrations [5–7].

It is interesting that the nitrogen analogue (**1b**) with the pyrrole ring, which is very similar to furan in its ground state reactions, follows a distinctly different mechanism in the excited state and gives **3** by intermolecular addition of the pyrrole to a double bond [9]. No intramolecular formation of a bicyclic product was observed, as we expected on analogy with furan derivatives [1,8]. The bimolecular photoaddition does not occur upon irradiation of the *N*-methylpyrrole derivative (**1d**) and only traces of the bicyclo[3.2.1]octadiene product (**2b**) were formed [9]. We proposed [9] that the formation of dimeric product (**3**) occurs via photoinduced electron transfer, followed by proton transfer and radical combination, a mechanism analogous to the pyrrole addition to benzene [14–16], naphthalene [17,18] and stilbene [19,20]. Gilbert and co-workers [21] reported lately the intermolecular photoaddition of the pyrrole to styrene and stilbene and explained the process by similar mechanism.

The fact that the *N*-methylpyrrole derivative (**1d**), the compound without hydrogen transfer ability, gives intramolecular reaction forming bicyclo[3.2.1]octadiene product (**2b**), encouraged us to study the other *N*-substituted pyrrole derivatives but with an electron withdrawing group. In this paper, results from the irradiation of acyl derivatives (**5a**–**d**) are described.

2. Experimental

2.1. General

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 and 75 MHz,

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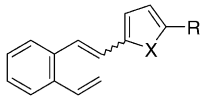
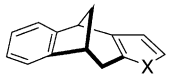
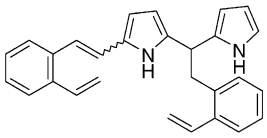


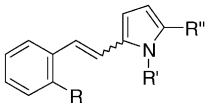
1 a: X = O; R = H
b: X = NH; R = H
c: X = NH; R = CH_3
d: X = NCH_3; R = H



2 a: X = O; R = H
b: X = NCH_3; R = H



3



4 a: R = CH_3; R' = R'' = H
b: R = CH_3; R' = CH_3; R'' = H
c: R = CH_3; R' = H; R'' = CH_3
5 a: R = $CH{=}CH_2$; R' = $COCH_3$; R'' = H
b: R = CH_3; R' = $COCH_3$; R'' = H
c: R = $CH{=}CH_2$; R' = COPh; R'' = H
d: R = CH_3; R' = COPh; R'' = H

Scheme 1.

respectively, in $CDCl_3$ and in C_6D_6 with Me_4Si as an internal standard. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. IR spectra were obtained with a Nicolet Magna-IR 760 FT-IR spectrometer. Mass spectra were recorded on Auto Spec Q (VG Analytical Manchester, GB) using EI technique. UV spectra were measured on Perkin-Elmer LAMBDA 20 spectrophotometer. Standard column chromatography was carried out on silica gel 60–230 meshes ASTM. Thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Elemental analyses were carried out in the Microanalytical Laboratory at the Rugjer Boskovic Institute. Melting points were obtained on an Original Kofler Mikroheiztisch apparatus (Reicherdt, Wien) and are uncorrected. Irradiations were performed in a quartz or Pyrex vessel in benzene solutions and in the Rayonet reactor equipped with RPR 3000 or 3500 A lamps, respectively. All irradiation experiments were carried out in degassed solutions made so by bubbling a stream of nitrogen or argon prior to irradiation.

Voltammetric measurements were performed using a MA-5450 potentiostat (Iskra, Slovenia) connected to external function generator. All experiments were carried out in a conventional three-electrode cell with a Pt-disc as working electrode ($d = 1$ mm) and a Pt wire as counter electrode. Electrode potentials are referred to the Ag/AgCl/3.5 M KCl reference electrode with salt bridge filled with 3 M ammonium nitrate. Lithium perchlorate (1 M) was used as a supporting electrolyte. All experiments were carried out in acetonitrile at room temperature and under nitrogen atmosphere.

Ionisation potentials were measured by photoelectron spectroscopy using a UPG200 instrument of Leybold-Heraeus equipped with a He (I) radiation source (21.21 eV). Samples were evaporated directly into the target chamber. In order to reach sufficient vapour pressure temperatures of 100–200 °C were necessary. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionisation energies, for broad and overlapping signals it was only ±0.1 eV.

2.2. Synthesis of the starting compounds (*5a–d*)

New acyl derivatives (**5a**, **c**, **d**) and the **5b** [12] for the irradiation experiments are prepared from the corresponding styrylpyrrole derivatives (**1b** and **4a**, respectively). Styrylpyrrole derivatives **1b** and **4a** [9], **4b** and **1c** [10,11], as well as **4c** [13] are prepared according to the described method. The isomers are separated by column chromatography and the pure *cis*- and *trans*-**1b** or -**4a**, respectively, are acylated following the known procedures [12,22–24].

*Cis-N-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (cis-**5a**).* Yield: 23.8% of colourless oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 241 (17996), 306 (7174); ^1H NMR (C_6D_6), δ (ppm): 7.47 (d, 1H, $J = 12.0$ Hz), 7.45–7.50 (m, 1H), 7.29–7.24 (m, 1H), 7.09–6.94 (m, 3H), 6.56 (d, 1H, $J = 12.0$ Hz), 6.35 (m, 1H), 5.94 (m, 1H), 5.72 (m, 1H), 5.58 (dd, 1H, $J = 17.4$, 1.2 Hz), 5.08 (dd, 1H, $J = 11.1$, 1.2 Hz), 1.72 (s, 3H, CH_3); ^{13}C NMR (C_6D_6), δ (ppm): 169.41 (s), 137.87 (s), 136.76 (s), 132.74 (s), 135.83 (d), 130.06 (d), 128.23 (d), 127.91 (d), 127.91 (d), 126.08 (d), 124.08 (d), 121.25 (d), 116.11 (d), 115.22 (t), 112.45 (d), 23.74 (q).

*Trans-N-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (trans-**5a**).* Yield: 48.7% of colourless oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 246 (11856), 330 (7544); IR (KBr), ν_{max} (cm^{-1}): 2924, 1716 (CO); ^1H NMR (C_6D_6), δ (ppm): 8.11 (d, 1H, $J = 16.2$ Hz), 7.67–7.63 (m 1H), 7.33–7.30 (m, 1H), 7.33 (d, 1H, $J = 16.2$ Hz), 7.09 (dd, 1H, $J = 17.4$, 11.0 Hz), 6.45 (m, 1H), 6.44 (m, 1H),

6.00 (m, 1H), 5.52 (dd, 1H, J = 17.4, 1.2 Hz), 5.18 (dd, 1H, J = 11.0, 1.2 Hz), 1.69 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 169.62 (s), 137.09 (s), 136.50 (s), 136.04 (s), 135.95 (d), 128.74 (d), 128.14 (d), 127.32 (d), 127.17 (d), 127.17 (d), 123.43 (d), 122.16 (d), 116.68 (t), 112.53 (d), 112.15 (d), 23.75 (q); MS, *m/z* (relative intensity): 237 (M^+, 12), 194 (33), 137 (41), 132 (71), 103 (43), 95 (84), 94 (100), 78 (33); HRMS calcd. for $C_{16}H_{15}NO$: 237.114815, found 225.113002. Anal. calcd. for $C_{16}H_{15}NO$: C, 80.98%; H, 6.37%; N, 5.90%. Found: C, 80.74%; H, 6.35%.

*Cis-N-benzoyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (cis-**5c**)*. Yield 73.3% of colourless oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 239.6 (25088), 312.7 sh (7608); IR (neat), ν_{max} (cm^{-1}): 1696 (CO); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.73 (d, 2H, J = 7.5 Hz), 7.50–7.62 (m, 2H), 7.48 (dd, 2H, J = 7.2, 7.5 Hz), 6.98 (d, 1H, J = 12 Hz), 6.94 (dd, 1H, J = 11.1, 17.7 Hz), 6.78 (d, 1H, J = 3.3 Hz), 6.59 (d, 1H, J = 12 Hz), 5.98 (dd, 1H, J = 3.3, 3.6 Hz), 5.88 (d, 1H, J = 3.3 Hz), 5.66 (dd, 1H, J = 1.2, 17.7 Hz), 5.22 (dd, 1H, J = 1.2, 11.1 Hz); ^{13}C NMR ($CDCl_3$), δ (ppm): 168.95 (s), 136.61 (s), 135.78 (s), 134.81 (d), 133.86 (s), 132.48 (d), 132.16 (s), 129.85 (d, 2C), 129.09 (d), 128.27 (d, 2C), 127.57 (d), 127.27 (d), 127.18 (d), 125.19 (d), 123.36 (d), 121.69 (d), 115.36 (d), 114.86 (t), 111.23 (d); MS, *m/z* (relative intensity): 315 (M^+, 100), 194 (17); HRMS calcd. for $C_{21}H_{17}NO$: 299.130465, found 299.142688.

*Trans-N-benzoyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (trans-**5c**)*. Yield: 96.3% of colourless oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 240.5 (16652), 321.8 sh (9754); IR (neat), ν_{max} (cm^{-1}): 1695 (CO); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.75 (d, 2H, J = 7.2 Hz), 7.15–7.62 (m, 9H), 7.09 (dd, 1H, J = 11.1, 17.4 Hz), 6.91 (d, 1H, J = 3.3 Hz), 6.71 (d, 1H, J = 3.3 Hz), 6.24 (dd, 1H, J = 3.3, 3.6 Hz), 5.63 (dd, 1H, J = 1.2, 17.4 Hz), 5.35 (dd, 1H, J = 1.2, 11.1 Hz); ^{13}C NMR ($CDCl_3$), δ (ppm): 169.17 (s), 136.05 (s), 135.30 (s), 135.20 (s), 134.85 (d), 133.83 (s), 132.52 (d), 129.82 (d, 2C), 128.34 (d, 2C), 127.69 (d), 127.30 (d), 126.37 (d), 126.06 (d), 125.64 (d), 124.19 (d), 121.25 (d), 116.34 (t), 111.58 (d), 111.46 (d). Anal. calcd. for $C_{21}H_{17}NO$: C, 84.25%; H, 5.72%; N, 4.68%. Found: C, 84.18%; H, 6.03%.

*Cis-N-benzoyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (cis-**5d**)*. Yield: 89.4% of colourless oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 206.0 (25551), 235.1 (21280), 260.0 (15118); IR (neat), ν_{max} (cm^{-1}): 1697 (CO); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.77 (d, 2H, J = 7.8 Hz), 6.31 (dd, 1H, J = 7.2, 7.5 Hz), 7.51 (dd, 2H, J = 7.5, 7.8 Hz), 7.32 (d, 1H, J = 7.2 Hz), 7.10–7.24 (m, 3H), 6.97 (d, 1H, J = 12.3 Hz), 6.84 (m, 1H), 6.58 (d, 1H, J = 12.3 Hz), 6.05 (dd, 1H, J = 3.3, 3.0 Hz), 5.95 (d, 1H, J = 3.0 Hz), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm): 168.87 (s), 137.29 (s), 135.83 (s), 133.83 (s), 132.45 (d), 132.30 (s), 129.83 (d), 129.83 (d, 2C), 128.47 (d), 128.20 (d, 2C), 127.84 (d), 126.96 (d), 125.57 (d), 123.26 (d), 120.78 (d), 114.84 (d), 111.12 (d), 19.56 (q); MS, *m/z* (relative intensity): 287 (M^+, 66), 182 (100); HRMS calcd. for $C_{20}H_{17}NO$: 287.130465, found 287.134597. Anal. calcd. for $C_{20}H_{17}NO$: C, 83.59%; H, 5.96%; N, 4.87%. Found: C, 83.29%; H, 5.98%; N, 5.21%.

*Trans - N - benzoyl - 2-[2-(2-methylphenyl)ethenyl]pyrrole (trans-**5d**)*. Yield: 82.2% of colourless oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 238.0 (13034), 328.1 (17572); IR (neat), ν_{max} (cm^{-1}): 1695 (CO); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.81 (d, 2H, J = 7.5 Hz), 7.65 (dd, 1H, J = 7.2, 7.5 Hz), 7.48–7.58 (m, 4H), 7.10–7.30 (m, 2H), 7.20 (d, 1H, J = 16.8 Hz), 7.18 (d, 1H, J = 16.8 Hz), 6.96 (d, 1H, J = 3.0 Hz), 6.76 (d, 1H, J = 3.3 Hz), 6.26 (dd, 1H, J = 3.3, 3.0 Hz), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$), δ (ppm): 169.22 (s), 136.14 (s), 135.42 (s), 135.36 (s), 133.91 (s), 132.52 (d), 130.19 (d), 129.83 (d, 2C), 128.36 (d, 2C), 127.18 (d), 126.01 (d), 125.87 (d), 125.30 (d), 124.12 (d), 120.32 (d), 111.46 (d), 19.84 (q).

2.3. Irradiation experiments

A degassed benzene solution (ca. 5×10^{-3} M) of a starting compound (**5a** or **5b**) was irradiated for 1 h at 300 nm. Solvent was removed in vacuum and the residue was column chromatographed on silica gel using petroleum ether–dichloromethane as eluent. Enriched fractions with various photoproducts were subjected to repeated thin layer chromatographic separations and the following compounds are isolated: starting compounds, **5a** or **5b**, respectively, were recovered in 4–6% yield and the photoproducts (**6a**, **7a**–**9a**, **10a** or **6b**, **7b**–**9b**, **10b**, **11**–**15**, respectively) in total yield of ∼20%. The rest were high-molecular weight materials with some unidentified structures in quantities too small to be analysed.

Cis- and *trans*-2-[2-(2-vinylphenyl)ethenyl]pyrrole (*cis-* and *trans*-**6a**) [9]: 5.2% (9:1).

Cis- and *trans*-2-[2-(2-methylphenyl)ethenyl]pyrrole (*cis-* and *trans*-**6b**) [9]: 2.2% (9:1).

*Cis-3-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (cis-**7a**)*: 1.4%, oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 333.3 (7613); IR (neat), ν_{max} (cm^{-1}): 3300 (NH), 1651 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.91 (d, 1H, J = 12.3 Hz), 7.70 (br s, 1H, NH), 6.90–7.45 (m, 4H), 6.81 (dd, 1H, J = 17.4, 11.1 Hz), 6.39 (d, 1H, J = 12.3 Hz), 6.16 (dd, 1H, J = 2.4, 2.7 Hz), 5.59 (dd, 1H, J = 2.4, 2.7 Hz), 5.51 (dd, 1H, J = 17.4, 1.2 Hz), 5.03 (dd, 1H, J = 11.1, 1.2 Hz), 2.20 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 194.43 (s), 137.23 (s), 137.03 (s), 135.01 (d), 132.77 (s), 129.83 (d), 129.48 (d), 129.15 (d), 127.55 (d), 126.45 (d), 123.85 (s), 122.37 (d), 118.48 (d), 116.24 (t), 111.38 (d), 28.86 (q); MS, *m/z*: 237 (M^+, 45), 222 (40), 194 (65), 122 (100).

*Trans-3-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (trans-**7a**)*: 0.9%, oil; UV (EtOH), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 243.1 (18645), 362.3 (17063); IR (neat), ν_{max} (cm^{-1}): 3282 (NH), 1624 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 8.27 (d, 1H, J = 16.8 Hz), 6.90–7.70 (m, 6H), 6.80 (d, 1H,

J = 16.8 Hz), 6.32 (dd, 1H, J = 2.4, 2.7 Hz), 6.01 (dd, 1H, J = 2.4, 2.7 Hz), 5.53 (dd, 1H, J = 16.2, 1.2 Hz), 5.23 (dd, 1H, J = 10.8, 1.2 Hz), 2.23 (s, 3H).

*Cis-3-acetyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (cis-**7b**)*: 1.6%, m.p. 79 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 252.0 (8425), 331.0 (10071); IR (neat), ν_{max} (cm^{-1}): 3300 (NH), 1645 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.89 (d, 1H, J = 12.3 Hz), 7.81 (br s, 1H, NH), 7.06 (d, 1H, J = 7.2 Hz), 6.86–7.00 (m, 3H), 6.33 (d, 1H, J = 12.3 Hz), 6.19 (dd, 1H, J = 2.4, 2.7 Hz), 5.64 (dd, 1H, J = 2.4, 2.7 Hz), 2.21 (s, 3H), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR (C_6D_6), δ (ppm): 194.39 (s), 138.16 (s), 137.20 (s), 133.08 (s), 131.23 (d), 129.09 (d), 128.52 (d), 128.20 (d), 126.99 (d), 123.69 (s), 121.59 (d), 118.28 (d), 111.39 (d), 28.89 (q), 19.83 (q); MS, *m/z*: 225 (M^+, 100), 210 (56), 182 (71), 167 (54), 134 (26), 115 (23).

*Trans-3-acetyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (trans-**7b**)*: 1.1%, oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 257.7 (5029), 359.6 (7040); IR (neat), ν_{max} (cm^{-1}): 3289 (NH), 1633 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 8.27 (d, 1H, J = 16.8 Hz), 7.67 (m, 1H), 7.60 (br s, 1H, NH), 6.98–7.20 (m, 3H), 6.72 (d, 1H, J = 16.8 Hz), 6.34 (dd, 1H, J = 2.4, 2.7 Hz), 6.03 (dd, 1H, J = 2.4, 2.7 Hz), 2.23 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 136.74 (s), 130.98 (d), 127.71 (d), 127.35 (d), 126.60 (d), 126.34 (d), 123.10 (s), 120.94 (d), 118.50 (d), 112.18 (d), 28.83 (q), 20.17 (q) (three singlets are too small to be seen).

*Cis-4-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (cis-**8a**)*: 0.9%, m.p. 85 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 239.6 (23526), 289.3 sh (11047); IR (KBr), ν_{max} (cm^{-1}): 3193 (NH), 1627 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.44 (d, 1H, J = 7.5 Hz), 6.93–7.24 (m, 4H), 6.87 (dd, 1H, J = 17.7, 11.1 Hz), 6.60 (m, 1H), 6.20 (m, 1H), 6.18 (d, 1H, J = 12.0 Hz), 6.11 (d, 1H, J = 12.0 Hz), 5.56 (dd, 1H, J = 17.7, 1.2 Hz), 5.09 (dd, 1H, J = 11.1, 1.2 Hz), 2.04 (s, 3H); MS, *m/z*: 237 (M^+, 100).

*Cis-4-acetyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (cis-**8b**)*: 1.6%, m.p. 108 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 237.5 (15005), 290.0 (8501); IR (neat), ν_{max} (cm^{-1}): 3190 (NH), 1625 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.60 (br s, 1H, NH), 6.94–7.07 (m, 4H), 6.61 (m, 1H), 6.24 (m, 1H), 6.14 (s, 2H), 2.05 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 192.02 (s), 137.96 (s), 137.20 (s), 131.22 (s), 131.20 (d), 129.20 (d), 128.57 (d), 127.35 (s), 126.94 (d), 125.09 (d), 124.19 (d), 121.13 (d), 111.85(d), 27.03 (q), 19.91 (q); MS, *m/z*: 225 (M^+, 100).

*Cis-5-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (cis-**9a**)*: 2.9%, m.p. 108 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 241.0 (16255), 334.1 (23612); IR (KBr), ν_{max} (cm^{-1}): 3266 (NH), 1634 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 9.20 (br s, 1H, NH), 7.45 (d, 1H, J = 7.5 Hz), 7.00–7.20 (m, 3H), 6.85 (dd, 1H, J = 17.4, 11.1 Hz), 6.37 (d, 1H, J = 12.0 Hz), 6.32 (dd, 1H, J = 2.7, 3.6 Hz), 6.14 (d, 1H, J = 12.0 Hz), 5.90 (dd, 1H, J = 2.7, 3.6 Hz), 5.55 (dd, 1H, J = 17.4, 1.2 Hz), 5.06 (dd, 1H, J = 11.1, 1.2 Hz), 1.91 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 187.20 (s), 136.86 (s), 136.64 (s), 135.74 (s), 135.26 (d), 132.69 (s), 129.48 (d), 129.15 (d), 128.89 (d), 128.83 (d), 126.46 (d), 121.70 (d), 117.42 (d), 115.94 (t), 112.82 (d), 25.11 (q); MS, *m/z*: 237 (M^+, 90), 194 (65), 122 (100).

*Trans-5-acetyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (trans-**9a**)*: 4.4%, m.p. 131 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 251.1 (11095), 357.0 (26658); IR (KBr), ν_{max} (cm^{-1}): 3264 (NH), 1632 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 10.00 (br s, 1H, NH), 7.30–7.42 (m, 2H), 7.31 (d, 1H, J = 16.0 Hz), 7.02–7.10 (m, 2H), 6.96 (dd, 1H, J = 17.4, 10.8 Hz), 6.55 (dd, 1H, J = 3.6, 2.4 Hz), 6.52 (d, 1H, J = 16.0 Hz), 6.21 (dd, 1H, J = 3.6, 2.4 Hz), 5.52 (dd, 1H, J = 17.4, 1.2 Hz), 5.15 (dd, 1H, J = 10.8, 1.2 Hz), 2.08 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 187.79 (s), 138.41 (s), 137.23 (s), 136.12 (s), 135.66 (d), 133.17 (s), 128.51 (d), 128.50 (d), 127.88 (d), 127.25 (d), 126.97 (d), 121.11 (d), 119.05 (d), 116.77 (t), 110.56 (d), 25.34 (q).

*Cis-5-acetyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (cis-**9b**)*: 5.1%, m.p. 104–106 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 332.5 (22724); IR (neat), ν_{max} (cm^{-1}): 3268 (NH), 1633 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 9.99 (br s, 1H, NH), 7.27 (d, 1H, J = 6.9 Hz), 7.10–7.00 (m, 3H), 6.42 (d, 1H, J = 12.0 Hz), 6.38 (d, 1H, J = 12.0 Hz), 6.38 (dd, 1H, J = 3.3, 3.0 Hz), 5.97 (dd, 1H, J = 3.3, 3.0 Hz), 2.06 (s, 3H), 1.95 (s, 3H, $COCH_3$); ^{13}C NMR (C_6D_6), δ (ppm): 187 65 (s), 138.04 (s), 136.72 (s), 136.63 (s), 132.69 (s), 131.31 (d), 130.32 (d), 129.25 (d), 128.90 (d), 127.12 (d), 121.37 (d), 118.16 (d), 112.53 (d), 25.40 (q), 20.11 (q); MS, *m/z*: 225 (M^+, 100), 210 (55), 182 (31), 167 (23), 81 (46), 69 (88), 57 (52), 55 (52).

*Trans-5-acetyl-2-[2-(2-methylphenyl)ethenyl]pyrrole (trans-**9b**)*: 2.7%, oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 354.9 (17256); IR (neat), ν_{max} (cm^{-1}): 3259 (NH), 1634 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 10.28 (br s, 1H, NH), 7.22 (d, 1H, J = 16.2 Hz), 6.98–7.13 (m, 4H), 6.70 (d, 1H, J = 16.2 Hz), 6.58 (dd, 1H, J = 2.7, 3.3 Hz), 6.29 (dd, 1H, J = 2.7, 3.3 Hz), 2.13 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 187.36 (s), 138.21 (s), 136.72 (s), 136.47 (s), 133.04 (s), 131.15 (d), 128.94 (d), 127.89 (d), 126.88 (d), 126.09 (d), 119.90 (d), 118.64 (d), 110.02 (d), 25.26 (q), 19.97 (q).

*Cis-2-[2-acetyl-2-(2-vinylphenyl)ethenyl]pyrrole (cis-**10a**)*: 3.8%, oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 241.9 (12854), 358.6 (18951); IR (neat), ν_{max} (cm^{-1}): 3305 (NH), 1651 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.75 (s, 1H, H_{et}), 7.48 (d, 1H, J = 7.8 Hz), 7.23 (br s, 1H, NH), 7.08 (dd, 1H, J = 6.6, 7.8 Hz), 7.01 (dd, 1H, J = 7.2, 7.5 Hz), 6.94 (d, 1H, J = 7.5 Hz), 6.69 (dd, 1H J = 17.4, 11.1 Hz), 6.15 (m, 1H), 5.96 (m, 2H), 5.50 (dd, 1H, J = 17.4, 1.2 Hz), 4.94 (dd, 1H, J = 11.1, 1.2 Hz), 1.96 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 196.71 (s), 137.84 (s), 137.75 (s), 134.83 (d), 132.29 (s), 131.17 (d), 129.31 (d), 129.31 (d), 129.14 (s), 129.06 (d), 126.39 (d), 123.43 (d), 117.88 (d), 116.33 (t), 111.24 (d), 27.75 (q); MS, *m/z*: 238 (MH^+, 20), 194 (12), 95 (35), 81 (52), 69 (100), 55 (69).

*Cis-2-[2-acetyl-2-(2-methylphenyl)ethenyl]pyrrole (cis-**10b**)*: 3.3%, oil; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 356.2 (14322); IR (neat), ν_{max} (cm^{-1}): 3296 (NH), 1634 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.50 (br s 1H, NH), 7.68 (s, 1H, H_{et}), 6.95–7.08 (m, 4H), 6.15 (m, 1H), 6.02 (m, 1H), 5.99 (dd, 1H, J = 2.7, 3.6 Hz), 1.98 (s, 6H); ^{13}C NMR (C_6D_6), δ (ppm): 196.68 (s), 138.56 (s), 137.77 (s), 133.37 (s), 131.35 (d), 130.61 (d), 129.09 (d), 128.91 (d), 127.48 (d), 123.32 (d), 117.77 (d), 111.10 (d), 27.25 (q), 19.57 (q); MS, *m/z*: 225 (M^+, 100), 210 (50), 182 (59), 167 (42), 115 (48), 67 (41).

*2-[1,2-Diacetyl-2-(2-methylphenyl)ethyl]pyrrole (**11**)*: 1.4%, m.p. 76 °C; UV (EtOH), λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 248.0 (299); IR (neat), ν_{max} (cm^{-1}): 3380 (NH), 1712 (CO); ^{1}H NMR (C_6D_6), δ (ppm): 7.03 (d, 1H, J = 7.2 Hz), 6.96 (dd, 1H, J = 6.8, 7.5 Hz), 6.89 (dd, 1H, J = 7.5, 7.2 Hz), 6.80 (d, 1H, J = 7.2 Hz), 6.10 (m, 1H), 5.96 (m, 1H), 5.70 (m, 1H), 4.67 (d, 1H, J = 11.1 Hz), 4.28 (d, 1H, J = 11.1 Hz), 2.09 (s, 3H), 1.82 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (C_6D_6), δ (ppm): 207.66 (s), 207.44 (s), 138.06 (s), 135.64 (s), 131.38 (d), 128.40 (d), 127.88 (d), 126.94 (d), 125.05 (s), 118.40 (d), 109.44 (d), 108.76 (d), 58.09 (d), 55.49 (d), 29.60 (q), 28.91 (q), 19.59 (q); MS, *m/z*: 269 (M^+, 32), 226 (40), 184 (56), 122 (100).

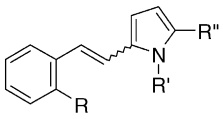
*2-Acetyl-7-methylbenzo[e]indole (**12**)* [12]: 1%, m.p. 243 °C; ^{1}H NMR ($CDCl_3$), δ (ppm): 9.39 (br s, 1H, NH), 8.13 (d, 1H, J = 7.8 Hz), 7.94 (d, 1H, J = 9.3 Hz), 7.72 (s, 1H), 7.54 (d, 1H, J = 9.3 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.33 (d, 1H, J = 7.2 Hz), 2.74 (s, 3H), 2.66 (s, 3H); MS, *m/z*: 223 (M^+, 100), 209 (73), 194 (55), 180 (45), 153 (57), 139 (52).

*2-[2-(2-Methylphenyl)ethyl]-3-acetylpyrrole (**13**)*: ^{1}H NMR (C_6D_6), δ (ppm): 7.00–7.20 (m, 5 H), 6.27 (dd, 1H, J = 2.4, 5.3 Hz), 5.91 (t, 1H, J = 2.7 Hz), 3.09 (m, 2H), 2.86 (m, 2H), 2.26 (s, 3H), 2.18 (s, 3H).

*2-[2-(2-Methylphenyl)ethyl]-5-acetylpyrrole (**14**)*: 0.9%, oil; IR (KBr), ν_{max} (cm^{-1}): 3273 (NH), 1632 (CO); ^{1}H NMR (C_6D_6), δ (ppm): ~9.9 (br s, 1H, NH), 6.80–7.20 (m, 4H), 6.58 (dd, 1H, J = 2.4, 3.3 Hz), 5.87 (dd, 1H, J = 2.4, 3.3 Hz), 2.64 (m, 2H), 2.55 (m, 2H), 2.09 (s, 3H), 2.00 (s, 3H); MS, *m/z*: 227 (M^+, 22), 184 ($M^+ - COCH_3$, 24), 136 (M^+ − acetylpyrrolyl, 35), 122 (100, methyltropylium).

*Traces of a mixture of cis- and trans-**15***: oil; from the ^{1}H NMR (C_6D_6) spectrum of the enriched fraction the characteristic signals of the compounds are: *cis*-**15**, δ (ppm): 6.26 (d, 1H, J = 11.7 Hz), 6.12–6.18 (m, 2H), 6.11 (d, 1H, J = 11.7 Hz), 5.92 (m, 1H), 5.23 (dd, 1H, J = 7.2, 8.1 Hz), 3.11 (dd, 1H, J = 7.2, 14.1 Hz), 2.95 (dd, 1H, J = 8.1, 14.1 Hz), 2.12 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H); *trans*-**15**, δ (ppm): 6.78 (d, 1H, J = 16.2 Hz), 6.39 (m, 1H), 6.18 (m, 1H), 6.07 (m, 1H), 5.85 (m, 1H), 4.95 (dd, 1H, J = 6.9, 7.8 Hz), 3.34 (dd, 1H, J = 6.9, 14.1 Hz), 3.26 (dd, 1H, J = 7.8, 14.1 Hz), 2.24 (s, 3H), 2.19 (s, 3H), 2.11 (s, 3H); MS, *m/z*: 408 (M^+, 5.9), 303 (51), 167 (38), 149 (100), 83 (38), 71 (49), 69 (57), 57 (72).

Table 1
Oxidation potentials of the substituted styrylpyrroles



Compound	R	R′	R″	E_{ox} (V)[a]	
				Cis	*Trans*
1b	Vinyl	H	H	0.86	0.74
4a	Me	H	H	0.84	0.71
4b	Me	Me	H	0.79	0.68
1c	Vinyl	H	Me	0.66	0.56
4c	Me	H	Me	0.64	0.54
5a	Vinyl	COMe	H	1.12	0.99
5d	Me	COPh	H	1.11	0.98
5e	Me	COOEt	H	1.10	0.99
5f	Me	COOPh	H	1.12	1.02

[a] In CH_3CN:H_2O/95:5% vs. Ag/AgCl/3.5 M KCl.

3. Results and discussion

3.1. General

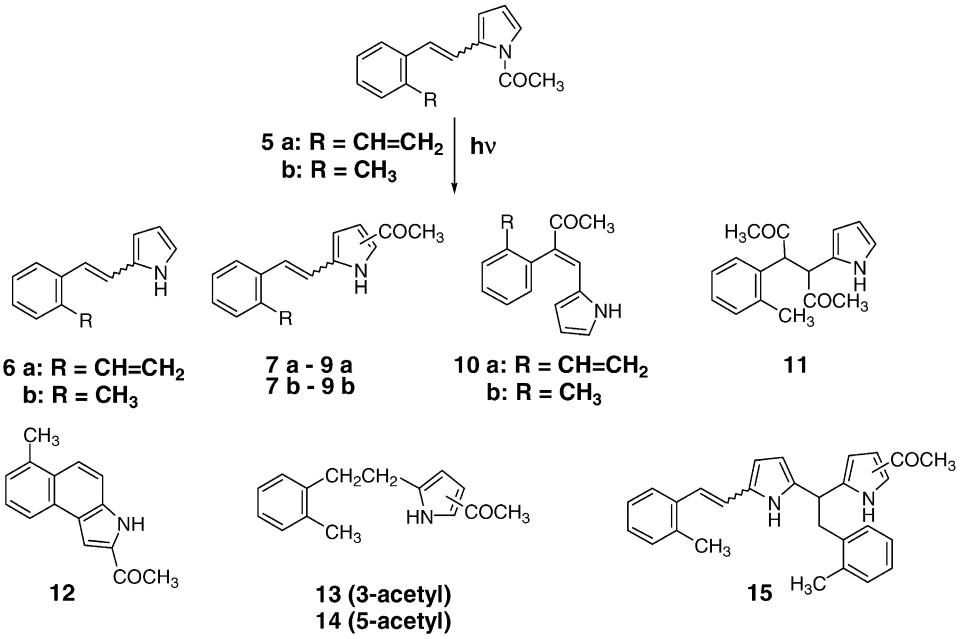
The idea was to substitute the nitrogen of the pyrrole ring with the electron withdrawing substituents that could not only prevent the proton transfer in styrylpyrrole derivatives but also increase the oxidation potential of the molecule in the ground state and thereby decrease the electron transfer aptitude of the molecule. Therefore several *N*-acyl derivatives were synthesized. As we can see from the measured oxidation potentials (Table 1), acyl derivatives of styrylpyrroles (**5a**, **d**–**f**) have higher oxidation potentials compared to their unsubstituted analogues for 0.25–0.30 V. The ionisation potential is also higher (Table 2) for acetyl derivative **5b** compared to the unsubstituted styryl derivatives.

Here we report the results of irradiation of *N*-acetyl (**5a**, **b**) and *N*-benzoyl (**5c**, **d**) derivatives of 2-styrylpyrroles. The irradiation was performed under anaerobic conditions at 300 and 350 nm, respectively. The fast conversion of the starting material and formation of a great number of the products was seen in the ^{1}H NMR spectrum of the crude reaction mixture already after a short period of time. It was obvious from the characteristic pattern of the vinyl group that no reaction with the vinyl group took place and no product as

Table 2
Ionisation potentials of the substituted styrylpyrroles

Compound	R	R′	R″	*IP* (eV)	
				Cis	*Trans*
1b	Vinyl	H	H	7.45	7.42
1c	Vinyl	H	Me	–	7.13
4a	Me	H	H	7.43[a]	7.41[a]
4b	Me	Me	H	7.43[a]	7.27[a]
4c	Me	H	Me	7.22[a]	7.13[a]
5b	Me	COMe	H	–	7.61

[a] From Ref. [13].

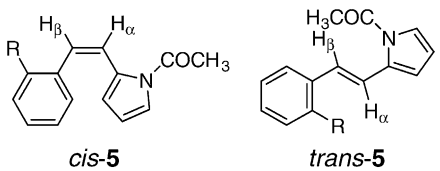


Scheme 2.

a result of intramolecular cycloaddition reaction of **5a** was found after careful chromatographic separation. To confirm that the vinyl group is not involved in the photoreaction and to facilitate the elucidation of numerous structures formed in the reaction (Scheme 2), the methyl derivative **5b** was irradiated under the same conditions. The same type of the products has been isolated and the structure confirmed by spectroscopic methods. The benzoyl derivatives (**5c**, **d**) were irradiated at the same conditions. Besides very much of tarry material, the ^{1}H NMR spectra of chromatographic fractions showed the presence of many photoproducts as in case of acetyl derivatives **5a** and **b**. No attempt was made to separate them. According to the ^{1}H NMR spectra of the enriched chromatographic fractions no intramolecular cycloaddition products have been seen.

3.2. Structure determination and mechanistic considerations

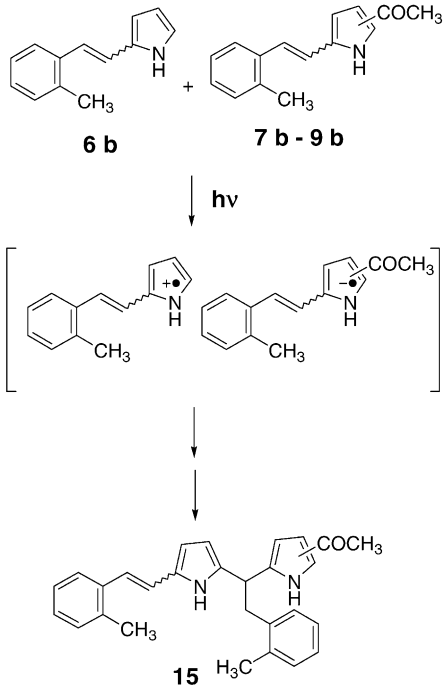
The structure of the photoproducts is based on their spectroscopic data combining different techniques. Comparing the chemical shifts of *N*-acylated (**5**) and non-acylated pyrrole derivatives (**6**) it is evident that the acetyl group, due to its anisotropy, induces the downfield shift of the ethene hydrogens. For an example: in *cis*-**5b** H_α is shifted for 1.16 ppm and in *trans*-**5b** H_β is shifted for 1.29 ppm.



The ^{1}H NMR spectra of 3-, 4- and 5-acetyl substituted pyrrole derivatives (**7**, **8** and **9**, respectively) show the NH signals as well as the signals of two CH-pyrrole hydrogens (instead of three in *N*-acylated compounds) on different positions and with different multiplicities indicating the position of acetyl group. The 3-acetyl isomer (**7**) shows characteristic downfield shift of ethene hydrogens, which is not seen in compounds **8** and **9**. Based on the value of the coupling constants of the pyrrole hydrogens, the structure of the 4- and 5-acetyl isomers is unambiguously assigned. The position of the acetyl group in the product **10** is assigned according to the presence of only one ethene hydrogen as a singlet and its LR COSY interaction with pyrrole hydrogen. The *E*-configuration was assigned comparing with the ^{1}H NMR spectra of the similar systems described in the literature [25–27]. The structure **11** is undoubtedly determined according to the molecular ion *m*/*z* 269, the presence of two acetyl groups and three CH-pyrrole signals in ^{1}H and ^{13}C NMR spectra as well as the absence of ethene signals and the presence of two aliphatic doubles (δ = 4–5 ppm). The structure of the product **12** was previously confirmed by X-ray analysis [12]. The products **13** and **14** differ from the products **7** and **9** in the absence of ethene signals and the presence of two aliphatic multiplets in the ^{1}H NMR spectra. The product **13** in comparison to **14** shows the downfield shift of the aliphatic multiplets in ^{1}H NMR spectrum indicating the position 3 of the acetyl group. Additional proof of the structure was obtained by mass spectrum. A small fraction of a mixture of two dimer isomers is also isolated. Due to the small quantities they could not be completely separated, but based on molecular ion and the characteristic ^{1}H NMR pattern which is comparable with the already known compound **3** [9], the dimeric structure

15 with non-specified acetyl position is assigned as drawn (Scheme 2).

As we managed to isolate various types of products in rather small quantities we suppose that there are several competing mechanisms leading to the detected products. The mechanism for the phototransposition of an acyl group from position 1 to 2 of the pyrrole ring has been presumed to involve dipolar intermediates [28]. On the other hand, analogous photo-Fries rearrangement [29] occurs through homolytic cleavage of the carbonyl–oxygen bond to give a caged radical pair. In-cage recombination affords acyl migration products, while hydrogen abstraction by the aryloxy radical leads to the formation of phenols, which are the most common by-products. In our case, according to products analyses, especially the formation of deacetylated products (**6**), and addition products (**11**, **13** and **14**), we may suggest that upon irradiation the C–N bond of the *N*-acetyl group is broken homolytically. Radicals formed in such a way could undergo in-cage recombination forming different phototransposition products (**7**–**10**) or may undergo cage escape giving secondary products such as crossover reduction products **11**, **13** and **14**. Some attempts have been made to determine the primary process, following the reaction course by measuring the UV or NMR spectra, but because of the fast and competitive processes no unambiguous conclusion could be made. Namely, within a short time, there are no detectable products. Within a reaction course too many products are detected. The formation of the product **15** with only one acetyl group could be explained as follows (Scheme 3): the formed deacylated product **6** (with the lower oxidation potential) undergoes photoinduced oxidation by the acylated molecules **7**, **8** or **9**, respectively (with the higher oxidation potential); the ion radical pair undergoes proton transfer and radical recombination [9,10] giving compound **15**.



Scheme 3.

As it is known from the literature [28] the phototransposition reaction of *N*-acetylpyrrole goes from the excited singlet state. In order to prevent phototransposition process and induce intramolecular cycloaddition that might go via triplet excited state, like in indole system [30–32], irradiation in the presence of benzophenone and acetone has been performed. No intramolecular cycloaddition products have been observed.

4. Conclusion

From the analysis of the isolated or detected products one can conclude that the following competing processes are operating under the formation of corresponding compounds (Scheme 2): deacetylation by Norrish I like cleavage (**6a**, **b**), phototransposition of the acetyl group and *cis–trans* isomerisation (**7a**, **b**–**10a**, **b**), oxidative electrocyclisation (**12**), addition to the double bond (**11**, **13**, **14**) as well as dimerisation of the primary rearranged products (**15**). No intramolecular cycloaddition process has been observed with vinyl derivatives (**5a** or **5d**) and formation of the bicyclo[3.2.1]octadiene structure like **2b**.

Based on the experiments the conclusion could be made that the phototransposition of the acetyl group is the main process.

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