JOC*Note*

Photochemical Formation of Novel Pyrrolo[3,2-*b*]-6,7-benzobicyclo[3.2.1]octa-2,6-diene

Nikola Basarić, Željko Marinić,[†] and
Marija Šindler-Kulyk*

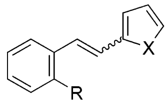
Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10 000 Zagreb, Croatia

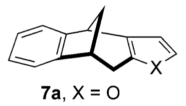
marija.sindler@fkit.hr

Received May 14, 2003

Abstract: The first synthesis of 1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (**11**) was achieved by the photochemical intramolecular [2 + 2] cycloaddition of *N*-phenoxycarbonyl- (**5a**) and *N*-ethoxycarbonyl-2-[2-(2-vinylphenyl)]pyrrole (**6a**), respectively, followed by basic hydrolysis of the isolated N-substituted 1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrroles (**10a**, **10b**). Some competitively formed products were also isolated.

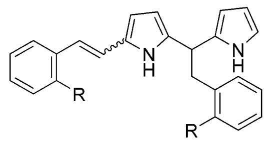
In continuation of our work on the synthesis and intramolecular photocycloaddition reactions of *o*-vinylstyrylfurans[1] to heteropolycyclic compounds, we studied the pyrrole analogues.[2] We found that, contrary to styrylfuran (**1**), which undergoes intramolecular [2 + 2] photocycloaddition, giving a bicyclo[3.2.1]octadiene structure (**7a**),[1a,f,h] the pyrrole analogue (**2a**) results in an intermolecular adduct that is formed by the addition of the pyrrole to a double bond.[2a] The nonparticipation of the *o*-vinyl group in this product formation was confirmed by the irradiation of *o*-methylstyrylpyrrole (**2b**) and subsequent isolation of a similar adduct (**8b**). The formation of dimeric products (**8a**,**b**) was explained[2a] by photoinduced electron transfer, followed by proton transfer and radical combination—a mechanism that is analogous to the pyrrole addition to benzene,[3] naphthalene,[4] and stilbene.[5] Gilbert et al.[6] have also reported the intermolecular photoaddition of the pyrrole ring to styrene and stilbene and explained the process by a similar mechanism.





7a, X = O
7b, X = NMe

1, X = O, R = vinyl
2a, X = NH, R = vinyl
2b, X = NH, R = Me
3, X = NMe, R = vinyl
4, X = NCOMe, R = vinyl
5a, X = NCOOPh, R = vinyl
5b, X = NCOOPh, R = Me
6a, X = NCOOEt, R = vinyl
6b, X = NCOOEt, R = Me

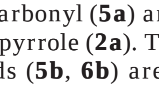


8a, R = vinyl
8b, R = Me

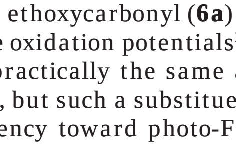
To obtain the [3.2.1] bicyclic system from pyrrole, the *N*-methyl-substituted pyrrole derivative **3**[2a] (a compound without hydrogen transfer ability) is irradiated. Intramolecular cycloaddition occurs, which results in a trace amount of a bicyclo[3.2.1]octadiene product (**7b**). When the *N*-acetyl derivative (**4**)[2g]—a compound with an electron-withdrawing group on the nitrogen and a higher oxidation potential than the *N*-methyl derivative (**3**)—is irradiated, no intramolecular cycloaddition or formation of a bicyclo[3.2.1]octadiene structure like **7b** is seen. Deacetylation by α-cleavage and phototransposition of the acetyl group were the main processes.[2g]

In an effort to find a process of obtaining pyrrolo-condensed benzobicyclo[3.2.1]octadiene, we introduced phenoxycarbonyl (**5a**) and ethoxycarbonyl (**6a**) groups to the styrylpyrrole (**2a**). The oxidation potentials[2g] of these compounds (**5b**, **6b**) are practically the same as that of the *N*-acetyl derivative (**4**), but such a substituent[7] would not have as great a tendency toward photo-Fries rearrangement. Moreover, this activating group could be easily removed after the cyclization process.

For the preparation of new starting compounds (**5a** and **6a**), an efficient method,[8] the acylation of **2a** (prepared[2a] by the Wittig reaction) with phenylchloroformate or ethylchloroformate, respectively, was done. The products were isolated and characterized[9] spectroscopically.



12



13

---

* To whom correspondence should be addressed.

[†] Current address: NMR Center, The Rugjer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia.

(1) (a) Šindler-Kulyk, M.; Špoljarić, L.; Marinić, Ž. *Heterocycles* **1989**, *29*, 679−682. (b) Šindler-Kulyk, M.; Metelko, B.; Stiplošek, Z. *Croat. Chem. Acta* **1989**, *62*, 81−87. (c) Šindler-Kulyk, M.; Stiplošek, Z.; Vojnović, D.; Metelko, B.; Marinić, Ž. *Heterocycles* **1991**, *32*, 2357−2363. (d) Šindler-Kulyk, M.; Kragol, G.; Piantanida, I.; Tomšić, S.; Vujković Cvijin, I.; Marinić, Ž.; Metelko, B. *Croat. Chem. Acta* **1996**, *69*, 1593−1602. (e) Vujković Cvijin, I.; Marinić, Ž.; Šindler-Kulyk, M. *Spectrosc. Lett.* **1998**, *31*, 989−1000. (f) Šindler-Kulyk, M.; Škorić, I.; Tomšić, S.; Marinić, Ž.; Mrvoš-Sermek, D. *Heterocycles* **1999**, *51*, 1355−1369. (g) Škorić, I.; Marinić, Ž.; Šindler-Kulyk, M. *Heterocycles* **2000**, *53*, 55−68. (h) Škorić, I.; Basarić, N.; Marinić, Ž.; Šindler-Kulyk, M. *Heterocycles* **2001**, *55*, 1889−1896.

(2) (a) Šindler-Kulyk, M.; Tomšić, S.; Marinić, Ž.; Metelko, B. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 476−479. (b) Basarić, N.; Tomšić, S.; Marinić, Ž.; Šindler-Kulyk, M. *Tetrahedron* **2000**, *56*, 1587−1593. (c) Basarić, N.; Marinić, Ž.; Šindler-Kulyk, M. *Tetrahedron Lett.* **2001**, *42*, 3641−3643. (d) Višnjevac, A.; Basarić, N.; Kojić-Prodić, B.; Šindler-Kulyk, M. *Acta Crystallogr. E* **2001**, *57*, 01252−01254. (e) Rademacher, P.; Basarić, N.; Kowski, K.; Šindler-Kulyk, M. *Eur. J. Org. Chem.* **2002**, 551−556. (f) Basarić, N.; Višnjevac, A.; Kojić-Prodić, B.; Griesbeck, A.; Šindler-Kulyk, M. *Photochem. Photobiol. Sci.* **2002**, *1*, 1017−1023. (g) Basarić, N.; Iveković, D.; Zimmermann, B.; Marinić, Ž.; Kowski, K.; Rademacher, P.; Šindler-Kulyk, M. *J. Photochem. Photobiol. A* **2003**, *154*, 123−130.

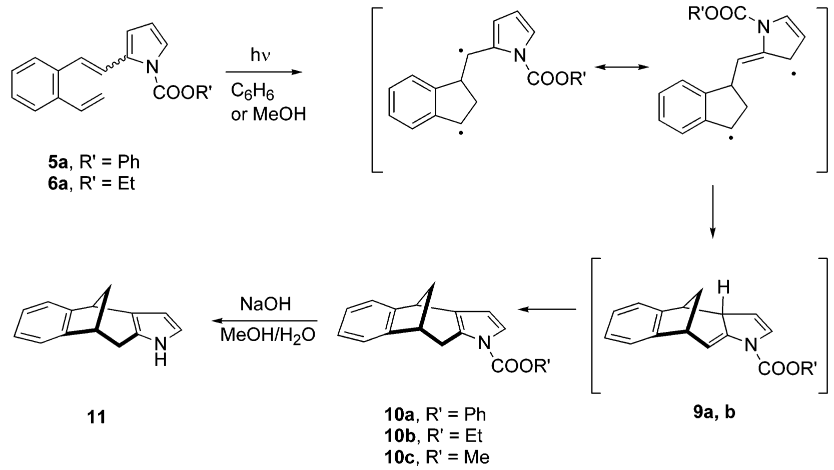
(3) (a) Bellas, M.; Bryce-Smith, D.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1967**, 263−264. (b) Bryce-Smith, D.; Clarke, M. T.; Gilbert, A.; Klunkin, G.; Manning, C. *Chem. Commun.* **1971**, 916−918. (c) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459−2489.

(4) (a) McCullough, J. J.; Huang, C. W.; Wu, W. S. *Chem. Commun.* **1970**, 1368−1369. (b) McCullough, J. J.; Wu, W. S.; Huang, C. W. *J. Chem. Soc., Perkin Trans. 2* **1972**, 370−375.

(5) (a) Kubota, T.; Sakurai, H. *Chem. Lett.* **1972**, 923−926. (b) Kubota, T.; Sakurai, H. *Chem. Lett.* **1972**, 1249−1250.

10.1021/jo0346454 CCC: $25.00

SCHEME 1



Benzene solutions of **5a** and **6a**, respectively, were irradiated under anaerobic conditions at 300 nm. After the chromatographic separation of the reaction mixture, the 50% starting compound **5a** (**6a**) was recovered, and 10% of the new compound, bicyclo[3.2.1]octadiene derivative **10a** (**10b**) (Scheme 1), was isolated and easily transformed to **11**. The formation of products **10** can be explained by an initial intramolecular cycloaddition that gives a 1,4-indan biradical, followed by the preferred cyclohexene ring closure to **9** and [1,3] hydrogen shift to **10**. Besides cycloaddition products **10**, various *o*-vinylstyryl pyrroles with the acyl group in different positions were obtained, but no attempt was made to isolate them. One of the phototransposition products (**12**) crystallized from the enriched chromatographic fraction, and it was identified.[9] Some traces of compound **13** were isolated that had formed because of oxygen addition to the intermediate product **9** (Scheme 1) and because of decomposition of the obtained peroxides during chromatographic separation, as in furan chemistry.[1h] Prolonged irradiation did not increase the yield of bicyclic compound **10a**, but decomposition resulted in a dark tarry material from which only diphenyloxalate was isolated. The presence of diphenyloxalate is a result of α-cleavage and recombination of the formed phenoxycarbonyl radicals, whereas the pyrrole radical fraction results in a high-weight material. The structure of the bicyclic products **10**, **11**, and **13** was determined by spectroscopic methods. The similarity of aliphatic protons pattern in ^{1}H NMR spectra[9] with the pattern of furan derivative **7a**[1a,f,h] definitively indicated a bicyclo[3.2.1]-octadiene structure.

To increase the yield of target bicyclic structures **10a** and **10b**, we have investigated photochemical reactions in acetonitrile and methanol. Weedon and et al. have reported[10,11] on solvent-dependent *N*-benzoyl- and *N*-ethoxycarbonylindole photochemistry. In our study, the change of solvent polarity by irradiation in acetonitrile did not influence the product ratios or reaction course. Protic solvent methanol only slowed the photochemical transformations of **5a** (**6a**). In the case of the irradiation of **5a** in methanol, in addition to the phenoxycarbonyl derivative **10a**, methoxycarbonyl derivative **10c** was isolated, as well as phenylmethyl carbonate and phenol. Their formation is explained by the thermal nucleophilic attack of methanol on the phenoxycarbonyl group that might occur in starting compound **5a** or in product **10a**—that is, by refluxing the compound **5a** in methanol, thermal transesterification is observed.

It is known that the photocycloaddition of indole analogues[10−12] proceeds via the triplet-excited state. In our experiments, the irradiation of **5a** (**6a**) in the presence of a triplet sensitizer resulted in the formation of high-molecular-weight material. As a consequence, we can conclude that our photocycloaddition proceeds via the singlet-excited state.

Monitoring the photochemical reaction course of *N*-phenoxycarbonyl derivative **5a** by ^{1}H NMR revealed cis−trans isomerization to be a major competing photochemical process that resulted in a photostationary state consisting of 60% cis and 40% trans isomer. Continuing the irradiation resulted in the characteristic signals for six protons of the intermediate **9a** appearing in the aliphatic region of the ^{1}H NMR spectrum[9] at 4.90, 3.87, 3.31, 3.21, and 2.03−2.30 ppm. The corresponding carbons[9] had doublets at 107.86, 49.57, 44.35, and 41.23 ppm and a triplet at 44.66 ppm. Any attempt to isolate the **9a** or **9b** resulted in its rearrangement to **10a** or **10b**, respectively, by [1,3] H-shift during the separation on silica gel.

Pyrrolobicyclo[3.2.1]octadiene (**11**) was obtained by the removal of the activating alkoxycarbonyl group from **10** under basic conditions. Although less stable than **10**, the target compound **11** was isolated and spectroscopically characterized.[9] This allowed us conclude that the alkoxycarbonyl group, as a substituent on the pyrrole nitrogen, is a convenient activating group for the intramolecular

---

(6) Austin, M.; Covell, Ch.; Gilbert, A.; Hendrickx, R. *Liebigs Ann./Recueil* **1997**, 943−946.

(7) Weedon, A. N−Phenoxycarbonylindole gives cyclopentene photocycloadducts in 75% yield. In *Photochemical Key Steps in Organic Synthesis*; Mattay, J., Griesbeck, A., Eds.; VCH: Weinheim, 1994; pp 163−167.

(8) Illi, V. O. *Synthesis* **1979**, 387−388.

(9) See the Supporting Information.

(10) Oldroyd, D. L.; Weedon, A. C. *J. Photochem. Photobiol. A* **1991**, *57*, 207−216.

(11) Weedon, A. C.; Zhang, B. *Synthesis* **1992**, 95−99.

(12) Andrew, D.; Hastings, D. J.; Oldroyd, D. L.; Rudoloh, A.; Weedon, A. C.; Wong, D. F.; Zhang, B. *Pure Appl. Chem.* **1992**, *64*, 1327−1334.

photocycloaddition reaction and formation of the pyrrolic condensed benzobicyclo[3.2.1]octadiene structure.

Experimental Section

Irradiation of *N*-Phenoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (5a). In Benzene. In a quartz vessel, 423 mg (1.34 mmol) of **5a**[9] was dissolved in 200 mL of benzene. The solution was then purged with argon and irradiated in a Rayonet reactor for 4 h at 300 nm. The solvent was removed, and the residue was chromatographed on silica gel using dichloromethane/petroleum ether as an eluent. This chromatographic separation resulted in 200 mg (47.3%) of the starting material **5a**, 10 mg (6.2%) of diphenyl oxalate, 35 mg (8.3%) of *N*-phenoxycarbonyl-1,4,9,10-tetrahydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]pyrrole (**10a**), and 60 mg (14.2%) of the phototransposition product mixture, whereas high molecular weight products remained on the column. From the phototransposition product mixture, 10 mg (2.4%) of *cis*-2-[2-phenoxycarbonyl-2-(2-vinylphenyl)ethenyl]pyrrole (**12**) precipitated as a yellowish solid in the C_6D_6 solution.

***N*-Phenoxycarbonyl-1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (10a).** This substance was a colorless solid, 35 mg (8.3%). Mp: 120 °C. IR (KBr)/cm^{-1}: 1754 (CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10−7.50 (m, 10H), 6.20 (d, 1H, $J = 3.3$ Hz), 3.87 (d, 1H, $J = 4.2$ Hz), 3.64 (dd, 1H, $J = 4.2$, 4.8 Hz), 3.42 (dd, 1H, $J = 4.8$, 17.7 Hz), 2.99 (d, 1H, $J = 17.7$ Hz), 2.51 (ddd, 1H, $J = 4.2$, 4.2, 10.2 Hz), 2.14 (d, 1H, $J = 10.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.52 (s), 150.80 (s), 150.00 (s), 148.88 (s), 144.94 (s), 129.71 (s), 129.43 (d, 2C), 126.25 (d), 126.15 (d, 2C), 126.03 (d), 123.58 (d), 121.25 (d), 120.76 (d), 120.35 (d), 109.90 (d), 41.91 (t), 40.16 (d), 40.08 (d), 32.00 (t). MS *m*/*z* (relative intensity): 315 (M^+, 32), 239 (56), 221 (100), 193 (36). HRMS (EI^+): calcd for $C_{21}H_{17}NO_2$ (M) 315.12593, found 315.13325. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.65; H, 5.48; N, 4.61. Found: C, 79.98; H, 5.43; N, 4.44.

***cis*-2-[2-Phenoxycarbonyl-2-(2-vinylphenyl)ethenyl]pyrrole (12).** This product was a yellowish solid, 10 mg (2.4%). Mp: 153−155 °C. IR (neat)/cm^{-1}: 3322 (NH), 1739 (CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.71 (d, 1H, $J = 7.2$ Hz), 7.58 (broad s, 1H), 7.00−7.45 (m, 8H), 6.79 (dd, 1H, $J = 10.5$, 17.7 Hz), 6.62 (m, 1H), 6.40 (m, 1H), 6.12 (m, 1H), 5.71 (dd, 1H, $J = 1.2$, 17.7 Hz), 5.23 (dd, 1H, $J = 1.2$, 10.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (singlets are not seen) 134.03 (d), 132.31 (d), 130.48 (d), 129.09 (d, 2C), 128.86 (d), 128.56 (d), 125.81 (d), 125.38 (d), 123.60 (d), 121.58 (d, 2C), 118.36 (d), 115.95 (t), 110.17 (d). MS *m*/*z* (relative intensity): 315 (M^+, 17), 222 (77), 194 (100). UV (EtOH): λ (ϵ) 242.0 (13 173), 348.2 (21 965).

***N*-Phenoxycarbonyl-1,4,9,10-tetrahydro-4,9-methano-10-*exo*-hydroxybenzo[4,5]cyclohepta[1,2-*b*]pyrrole (13).** This oily substance was produced only in trace amounts. IR (neat)/cm^{-1}: 3542 (OH), 1739 (CO). ^{1}H NMR (300 MHz, C_6D_6): δ 6.72−7.20 (m, 10H), 5.94 (d, 1H, $J = 3.3$ Hz), 4.99 (s, 1H), 4.09 (broad s, 1H), 3.74 (d, 1H, $J = 5.1$ Hz), 3.59 (d, 1H, $J = 4.2$ Hz), 2.70 (d, 1H, $J = 10.5$ Hz), 2.27 (ddd, 1H, $J = 4.2$, 5.1, 10.5 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 153.64 (s), 150.83 (s), 149.78 (s), 143.95 (s), 134.25 (s), 129.90 (d, 2C), 127.53 (d), 127.18 (d), 126.82 (d), 126.79 (d), 125.72 (d), 121.94 (d, 2C), 110.56 (d), 67.99 (d), 48.60 (d), 41.75 (d), 40.09 (t). MS *m*/*z* (relative intensity): 331 (M^+, 20), 314 (5), 77 (100).

In Methanol. In a quartz vessel, 294 mg (0.93 mmol) of *N*-phenoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (**5a**) was dissolved in 100 mL of methanol. The solution was purged with argon and irradiated in a Rayonet reactor at 300 nm for 6 h. The solvent was removed by distillation, and the residue was chromatographed on silica gel using petroleum ether/dichloromethane as an eluent. Chromatographic separation resulted in 12 mg (6.4%) of 2-[2-(2-vinylphenyl)ethenyl]pyrrole (**2a**), 70 mg (23.8%) of the starting material (**5a**), 36 mg (25.4%) of methylphenyl carbonate, 10 mg (3.4%) of *N*-phenoxycarbonyl-1,4,9,10-tetrahydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]pyrrole (**10a**), 15 mg (6.4%) *N*-methoxycarbonyl-1,4,9,10-tetrahydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]pyrrole (**10c**), and 42 mg (47.3%) of phenol. Trace amounts of phototransposition products, oxidation products, and high molecular weight material remained on the column.

***N*-Methoxycarbonyl-1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (10c).** This product was a colorless solid, 15 mg (6.4%). Mp: 59 °C. IR (KBr)/cm^{-1}: 1740 (CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, 1H, $J = 6.9$ Hz), 6.95−7.18 (m, 3H), 6.92 (d, 1H, $J = 3.3$ Hz), 5.99 (d, 1H, $J = 3.3$ Hz), 3.77 (s, 3H), 3.71 (d, 1H, $J = 4.2$ Hz), 3.50 (dd, 1H, $J = 4.2$, 5.1 Hz), 3.23 (dd, 1H, $J = 5.1$, 17.7 Hz), 2.80 (d, 1H, $J = 17.7$ Hz), 2.36 (ddd, 1H, $J = 4.2$, 4.2, 9.9 Hz), 1.98 (d, 1H, $J = 9.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.62 (s), 151.20 (s), 145.02 (s), 129.02 (s), 126.20 (d), 125.94 (d), 124.94 (s), 123.51 (d), 120.33 (d), 118.38 (d), 109.19 (d), 53.36 (q), 41.98 (t), 40.18 (d), 40.14 (d), 32.02 (t). MS *m*/*z* (relative intensity): 253 (M^+, 100), 221 (46), 211 (89), 193 (34), 167 (96). HRMS (EI^+): calcd for $C_{16}H_{15}NO_2$ (M) 253.11028, found M^+ 253.10616. Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.94; H, 6.01.

Irradiation of *N*-Ethoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (6a) in Benzene or Methanol. In a quartz vessel, 145 mg (0.40 mmol) of *N*-ethoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (**6a**) was dissolved in 100 mL of benzene or methanol. The solution was purged with argon and irradiated in a Rayonet reactor at 300 nm for 4 h in benzene or for 6 h in methanol. The solvent was removed by distillation, and the residue was chromatographed on silica gel using petroleum ether/dichloromethane as an eluent. Chromatographic separation furnished 66 mg (45.5%) of the starting material (**6a**), 17 mg (11.7%) of *N*-ethoxycarbonyl-1,4,9,10-tetrahydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]pyrrole (**10b**), and 32 mg (22.1%) of the phototransposition products. Oxidation products and high molecular weight material remained on the column.

***N*-Ethoxycarbonyl-1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (10b).** This substance was a colorless solid, 17 mg (11.7%). Mp: 76 °C. IR (KBr)/cm^{-1}: 1744 (CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, 1H, $J = 6.3$ Hz), 6.90−7.10 (m, 4H), 5.98 (d, 1H, $J = 3.3$ Hz), 4.22 (q, 2H, $J = 7.2$ Hz), 3.71 (d, 1H, $J = 4.2$ Hz), 3.49 (dd, 1H, $J = 4.5$, 5.1 Hz), 3.23 (dd, 1H, $J = 5.1$, 17.4 Hz), 2.80 (d, 1H, $J = 17.4$ Hz), 2.36 (ddd, 1H, $J = 4.5$, 5.1, 10.2 Hz), 1.98 (d, 1H, $J = 10.2$ Hz), 1.26 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.64 (s), 150.55 (s), 145.02 (s), 128.95 (s), 126.17 (d), 125.89 (d), 124.83 (s), 123.48 (d), 120.31 (d), 118.37 (d), 108.96 (d), 62.66 (t), 41.97 (t), 40.19 (d), 40.15 (d), 32.10 (t), 14.16 (q). MS *m*/*z* (relative intensity): 267 (M^+, 100), 239 (7), 194 (15). HRMS (EI^+): calcd for $C_{17}H_{17}NO_2$ (M) 267.12593, found 267.13087. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.18; H, 6.53.

Irradiation of *N*-Phenoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (5a) and *N*-Ethoxycarbonyl-2-[2-(2-vinylphenyl)ethenyl]pyrrole (6a), Respectively, in Benzene in the Presence of Benzophenone. In a kimax cuvette, 20 mg (0.063 mmol) of *cis*-**5a** or 20 mg (0.054 mmol) of **6a** was dissolved in 20 mL of benzene, 226 mg (1.27 mmol) or 216 mg (1.18 mmol) of benzophenone, respectively, was added, and the solution purged with argon. The reaction mixture was irradiated for 2 h at 350 nm, and solvent was removed by distillation. ^{1}H NMR spectra of the crude photochemical mixture revealed the formation of only high molecular weight material.

Removal of the Protecting Groups from the N-Substituted 1,4,9,10-Tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrroles (10a, 10b). A saturated solution of sodium hydroxide in methanol/water (2:1) was prepared, and 20 mg of *N*-ethoxycarbonyl (**10b**) or *N*-phenoxycarbonyl-1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (**10a**) was added to 3 mL of the solution. The reaction mixture was refluxed for 3 h, cooled, and extracted with dichloromethane. The solvent was removed from the dried dichloromethane extracts, and the residue was filtered through column of silica gel using dichloromethane. Filtration furnished 16 mg (80%) of 1,4,9,10-tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (**11**).

1,4,9,10-Tetrahydro-4,9-methanobenzo[4,5]cyclohepta[1,2-*b*]pyrrole (11). This product was a colorless oil, 16 mg (80%). IR (neat)/cm^{-1}: 3390 (NH). ^{1}H NMR (300 MHz, C_6D_6): δ

7.21 (d, 1H, $J = 6.3$ Hz), 7.13 (d, 1H, $J = 7.5$ Hz), 6.90−7.05 (m, 3H), 6.26 (broad s, 1H), 6.12 (d, 1H, $J = 2.7$ Hz), 3.82 (d, 1H, $J = 4.5$ Hz), 3.28 (dd, 1H, $J = 5.4$, 4.5 Hz), 2.70 (dd, 1H, $J = 5.4$, 5.3 Hz), 2.35 (ddd, 1H, $J = 4.5$, 4.5, 10.2 Hz), 2.25 (d, 1H, $J = 15.3$ Hz), 1.99 (d, 1H, $J = 10.2$ Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 153.93 (s), 145.78 (s), 127.09 (d), 126.27 (d), 124.71 (s), 123.98 (d), 121.71 (s), 121.37 (d), 115.52 (d), 105.38 (d), 44.13 (t), 41.44 (d), 41.41 (d), 30.37 (t). MS *m*/*z* (relative intensity): 196 (MH$^+$, 100), 195 (30, M$^+$). HRMS (EI$^+$): calcd $C_{14}H_{14}N$ (MH) 196.11262, found MH$^+$ 196.11961.

Acknowledgment. Financial support from the Ministry of Science and Technology of the Republic of Croatia under contracts 0125004 and 0098959 is gratefully acknowledged.

Supporting Information Available: Experimental procedures for the synthesis of the new starting compounds (**5a**,**b** and **6a**,**b**), analytical data and NMR assignments for the bicyclic photoproducts (**10a**−**c**, **11**, and **13**), and ^{1}H and ^{13}C NMR spectra for all new compounds (**5a**,**b**, **6a**,**b**, aliphatic region for **9a** intermediate, **10a**−**c**, **11**, and **13**), and ^{1}H NMR of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0346454