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New photoinduced intramolecular ring closure to a benzopentaleno–pyrrole derivative from 5,5′-dimethyl-2,2′-(*o*-phenylenedivinylene)dipyrrole

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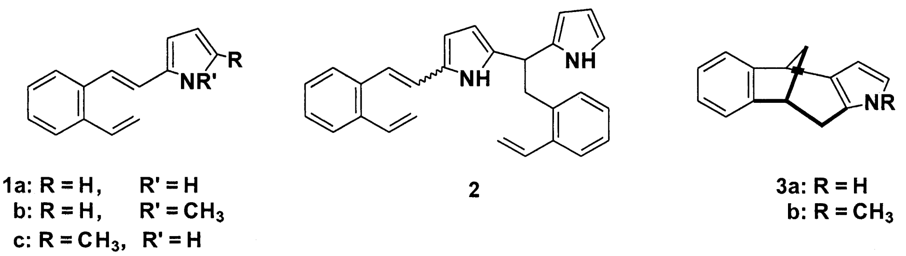
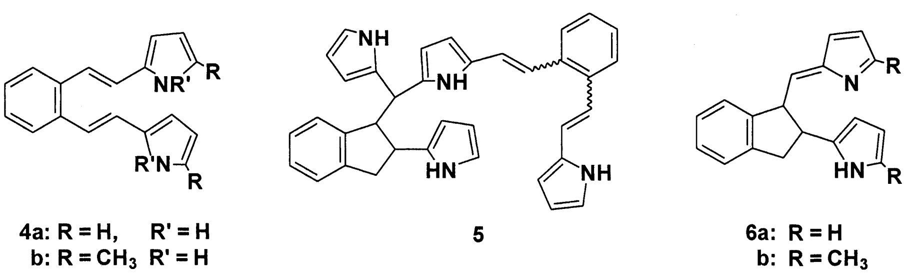
Abstract—New photochemically induced intramolecular cycloaddition and double cycloaddition of 5,5′-dimethyl-2,2′-(*o*-phenylenedivinylene)dipyrrole (**4b**) led to the formation of 2-{[2-(5-methyl-2-pyrrolyl)indan-1-ylidene]methinyl}-5-methylpyrrole (**8**) and 2-methyl-9-(5-methyl-2-pyrrolyl)-3b,4,8b,9-tetrahydro-4,5-benzopentaleno[1,2-*b*]pyrrole (**9**), respectively, in a 1:1 ratio. The compounds were characterized spectroscopically. Under the same conditions 5-methyl-2-(2-vinylphenylethenyl)pyrrole (**1c**) undergoes only *cis–trans* isomerization and decomposition. © 2001 Elsevier Science Ltd. All rights reserved.

In our previous papers[1,2] we described the first photoaddition reactions of styrylpyrroles in continuation of our interest on the synthesis[3,4] and photochemistry[5–9] of styrylfurans. Irradiation of **1a** gave **2** (Scheme 1) by regiospecific intermolecular addition of the pyrrole to the double bond.



Scheme 1.



Scheme 2.

Keywords: photochemistry; pyrroles.

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No intramolecular formation of the possible bicyclic product **3a** was observed,[1] as we had expected by analogy with furan derivatives.[5–7] The bimolecular photoaddition does not occur upon irradiation of **1b** and only traces of the bicyclic product **3b** were formed. The only tractable product formed came from *cis–trans* isomerization. We proposed[2] that the formation of the dimeric product **2** occurs via photoinduced electron transfer, followed by proton transfer and radical combination.

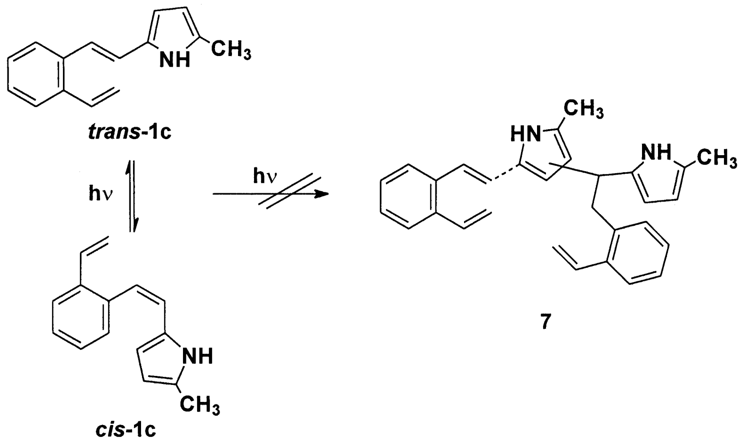
β,β′-Dipyrrolyl-*o*-divinylbenzene[2] (**4a**) (Scheme 2), containing two pyrrolyl–styryl groups in the same molecule, gave the dimeric product **5** presumably via intermediate **6a**. Traces of intramolecular products in the crude mixture were also observed after the irradiation, but they decompose during isolation and separation.

We blocked position 5 in the pyrrole moiety in an attempt to prevent the preferred nucleophilic attack of the starting compound. A methyl substituent was introduced in **1a** and **4a**. Herein, we report the photochemical behavior of 5-methyl-2-(2-vinylstyryl)pyrrole (**1c**) and 5,5′-dimethyl-2,2′-(*o*-phenylenedivinylene)dipyrrole (**4b**). The compounds **1c** and **4b**[10] are prepared by a Wittig 'one-pot' reaction[4] from the corresponding phosphonium salts and 5-methyl-2-pyrrolecarboxaldehyde (made by formylation[11] of 2-methylpyrrole[12]) following the procedure described for the preparation of **1a**, **1b**[1] and **4a**,[2] respectively.

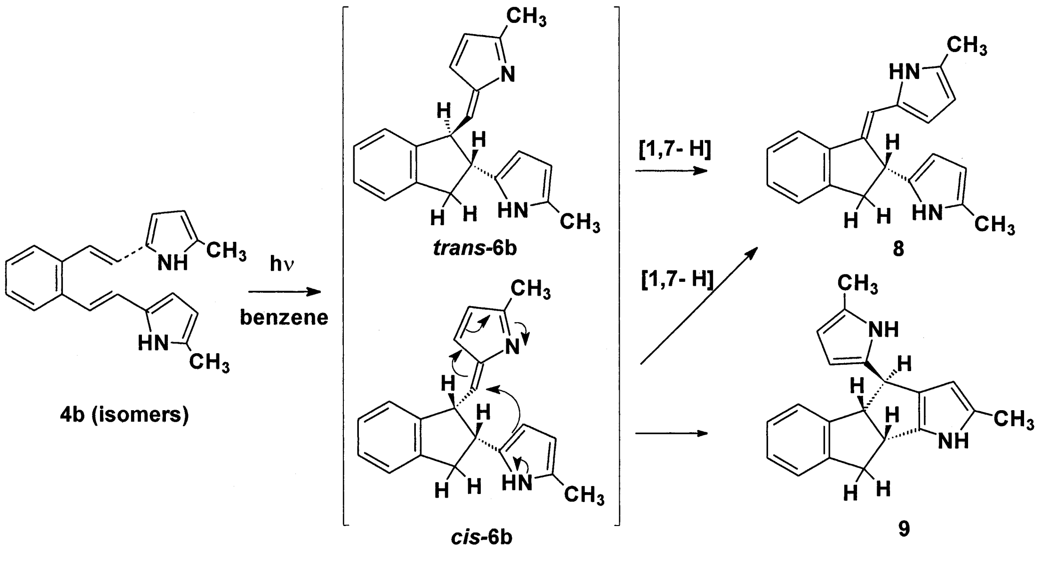
After irradiation of **1c** at 300 nm in benzene no intermolecular addition and formation of adduct **7** took place (Scheme 3). The only process observed was *cis–trans* isomerization, although it was accompanied by decomposition. Only more tarry material was observed with prolonged irradiation.

According to Gilbert[13] photoadditions of styrene and (*E*)-stilbene to 2-(1-phenylethyl)pyrroles occur at the 3- rather than the 5-position of the pyrrole moiety.

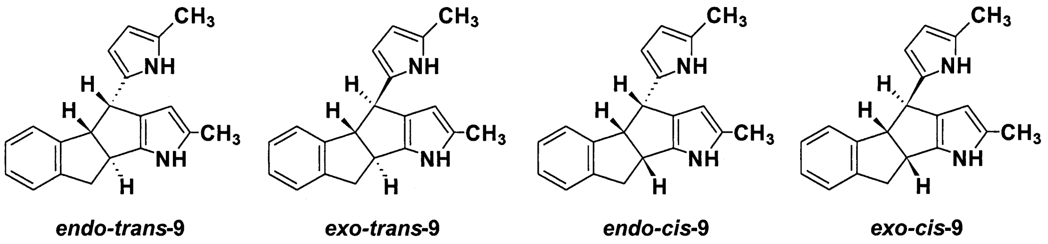
Irradiation of a 4×10^{-3} M benzene solution of **4b** at 350 nm gave the photoproducts **8** and **9** in a 1:1 ratio (Scheme 4), which were separated by column chro-



Scheme 3.



Scheme 4.



Scheme 5.

matography using neutral aluminum oxide and a petroleum ether/dichloromethane mixture as eluent.

Hydrogen transfer and regioselective ring closure in a *trans* and *cis* fashion follow the excitation and electron transfer[13–16] producing the intermediates *trans*-**6b** and *cis*-**6b**. The regioselectivity in product formation results from the charge distribution in the radical anion and the proton capture of the anionic center of the double bond at the position α to the benzene ring. Both *cis*- and *trans*-**6b** can undergo a 1,7-H shift to the more stable indanylidene product **8**, whereas, *cis*-**6b** undergoes a second intramolecular addition of the pyrrole moiety at the 3-position[13] giving the benzopentaleno–pyrrole derivative **9**. It is noteworthy that of the theoretically possible four isomers (Scheme 5), only one, *exo–cis* benzopentaleno–pyrrole derivative **9** is formed, probably due to thermodynamic reasons.

The structures of the photoproducts were established by ^{1}H and ^{13}C NMR using carbon–hydrogen and hydrogen–hydrogen 2D correlation spectra.[17] Product **8** has a narrow doublet at a low magnetic field (6.92 ppm) that is in accord with a similar conjugated system[18] which shows the allylic coupling with the indane hydrogen at 4.46 ppm. The corresponding carbon appears at 112.62 ppm in agreement with conjugated ethene derivatives.[1] The doublets of doublets at 3.54 ppm and 3.02 ppm, respectively, belong to the methylene hydrogens on the indane ring with the corresponding carbon at 41.12 ppm. The stereochemistry of the double bond was determined by NOESY experiments in which the interaction of the methylidene hydrogen and the aromatic hydrogen was observed. The benzopentaleno–pyrrole **9** shows five well-resolved signals: 4.48 (s), 4.38 (d), 3.70 (ddd), 3.01 (dd) and 2.79 (dd) ppm in the aliphatic region (C_6D_6). The signals at 4.38 ppm and 3.70 ppm belong to the hydrogens on the pentaleno bridge and are in the *cis* configuration based on NOESY experiments. The pyrrolyl substituent on the pentaleno moiety is *exo* oriented and the singlet at 4.48 ppm is assigned to the hydrogen connected to the carbon between the two pyrroles. In the *endo* orientation this hydrogen would appear in the ^{1}H NMR spectrum as a doublet because of the large vicinal *cis* coupling constant found in pentaleno derivatives.[19]

The formation of the *exo–cis* isomer **9** is supported by PM3 calculations. The isomer **9**, with *cis*-hydrogens on the pentaleno bridge and *exo*-orientation of the pyrrolyl group, is 25.30 kcal/mol more stable than the *endo–trans* isomer **9** which is, according to the calculations, the most unstable isomer.

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References

1. Šindler-Kulyk, M.; Tomšić, S.; Marinić, Ž.; Metelko, B. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 476–479.
2. Basarić, N.; Tomšić, S.; Marinić, Ž.; Šindler-Kulyk, M. *Tetrahedron* **2000**, *56*, 1587–1593.
3. Šindler-Kulyk, M.; Stiplošek, Z.; Metelko, B. *Croat. Chem. Acta* **1989**, *62*, 81–87.
4. Šindler-Kulyk, M.; Stiplošek, Z.; Vojnović, D.; Metelko, B.; Marinić, Ž. *Heterocycles* **1991**, *32*, 2357–2363.
5. Šindler-Kulyk, M.; Špoljarić, L.; Marinić, Ž. *Heterocycles* **1989**, *29*, 679–682.
6. Šindler-Kulyk, M.; Kragol, G.; Piantanida, I.; Tomšić, S.; Vujković Cvijin, I.; Marinić, Ž.; Metelko, B. *Croat. Chem. Acta* **1996**, *69*, 1593–1602.
7. Šindler-Kulyk, M.; Škorić, I.; Tomšić, S.; Marinić, Ž.; Mrvoš-Sermek, D. *Heterocycles* **1999**, *51*, 1355–1369.
8. Vujković Cvijin, I.; Marinić, Ž.; Šindler-Kulyk, M. *Spectrosc. Lett.* **1998**, *31*, 989–1000.
9. Škorić, I.; Marinić, Ž.; Šindler-Kulyk, M. *Heterocycles* **2000**, *53*, 55–68.
10. To be published later.
11. Silverstein, R. M.; Ryskiewicz, E. E.; Willard, C. *Org. Synth.* **1956**, *36*, 74–77.
12. Cornforth, J. W.; Firth, M. E. *J. Chem. Soc.* **1958**, 1091–1099.
13. Austin, M.; Covell, Ch.; Gilbert, A.; Hendrickx, R. *Liebigs Ann./Recueil* **1997**, 943–946.
14. Bellas, M.; Bryce-Smith, D.; Gilbert, A. *Chem. Commun.* **1967**, 263–264.
15. Bellas, M.; Bryce-Smith, D.; Gilbert, A. *Chem. Commun.* **1967**, 862–863.
16. Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459–2489.
17. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; John Wiley: New York, 1998; p. 212.
18. Hinz, W.; Jones, R. A.; Anderson, T. *Synthesis* **1986**, 620–623.
19. Kuck, D.; Eckrich, R.; Tellenbroeker, J. *J. Org. Chem.* **1994**, *59*, 2511–2515.