Pyrroles as C-nucleophiles in reactions with acylacetylenes

B. A. Trofimov, * Z. V. Stepanova, L. N. Sobenina, A. I. Mikhaleva, T. I. Vakul'skaya, V. N. Elokhina, I. A. Ushakov, D.-S. D. Toryashinova, and E. I. Kositsyna

Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, I ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 39 6046. E-mail: admin@irioch.irk.ru

The reactions of substituted pyrroles with terminal acylacetylenes occur selectively to form 2-(Z/E-2-acylvinyl) pyrroles. When the reactions are performed on the surface of silica gel, C-vinylation is noticeably accelerated to form predominantly *E*-isomers. ESR spectroscopy with the use of a spin trap demonstrated the ion-radical character of the process. The structures of the adducts synthesized, which exist as *anti-s-cis-* and *syn-s-cis-*rotamers, were studied by IR, UV, and NMR spectroscopy.

Key words: pyrroles, benzoylacetylene, thenoylacetylene, 2-(2-acylvinyl)pyrroles, oneelectron transfer, ion-radical pair, intramolecular hydrogen bond, Z/E-isomers, rotamer, conformation.

The reactions of pyrroles with activated acetylenes (only alkyl propiolates and acetylenedicarboxylates have been used to date in these reactions) can occur via different pathways, including Diels—Alder condensation and N- and C-nucleophilic attacks on a triple bond, depending on the structures of the initial reagents and reaction conditions.^{1,2}

Recently, we have demonstrated for the first time³ that pyrrole and 2-phenylpyrrole act exclusively as C-nucleophiles with respect to benzoylacetylene, which opens an unexpectedly simple and selective route to 2-acylvinylpyrroles.

The aim of the present work was to study this reaction further, to examine its scope, limitations, and selectivity, and to synthesize new 2-acylvinylpyrroles.

The reactions of pyrroles (1-5) with acylacetylenes (6 and 7) were performed under mild conditions (room temperature) in the absence of a solvent as well as in protic (methanol or ethanol) and aprotic (ether, benzene, hexane, or acetonitrile) solvents.

The reactions afforded predominantly Z-isomers of 2-(2-acylvinyl)pyrroles (8-15) in 52-87% yields. However, the Z-isomers were readily converted into the *E*-isomers in the course of isolation and purification or even upon storage in a solvent (compound Z-11 was converted into the *E*-isomer upon melting). Hence, the products were characterized primarily as mixtures of *E*- and Z-isomers (Table 1).

Monitoring of the addition of pyrrole 1 to benzoylacetylene 6 in methanol (an equimolar ratio of the reagents, room temperature) by UV spectroscopy showed that a long-wavelength band (396 nm) characteristic of the Z-isomer was observed in the initial stage of the reaction and then a band at $\lambda = 385$ nm appeared, which is indicative of isomerization of the Z-isomer to the



E-isomer. Therefore, the *Z*-isomer is a kinetically controlled product and the Z/E ratio is thermodynamically controlled.

The ease of the Z/E transformation, the control over the isomer ratio, and a decrease in the barrier to rotation about the C=C bond in the resulting adducts are the expected consequences of strong conjugation, weakening this bond:



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Com-	Isomer	M.p.	Found (%)			Molecular	IR, v/cm ⁻¹			
pound	(Z/E)	/°Ċ	Ca		N	formula	v(N-H)	v(C=O)	$\delta(=C-H)$	v(C=C)
8	E	131-134	<u>79.02</u> 79.16	<u>5.97</u> 5.62	<u>7.04</u> 7.10	C ₁₃ H ₁₁ NO	3259 w	1650	977	1547, 1565. 1586
	Ζ	98-99	<u>79.00</u> 79.16	<u>5.66</u> 5.62	$\frac{7.13}{7.10}$		3471 ^a w	1644	755	1541, 1579, 1574
9	$\frac{Z/E}{(1:5)}$	72-74	<u>80.30</u> 80.60	<u>7.91</u> 7.56	<u>5.65</u> 5.53	C ₁₇ H ₁₉ NO	3279	1640	974, 758	1542, 1586, 1598
10	$\frac{Z/E}{(1:5)}$	136-138	<u>81.85</u> 81.24	<u>7.09</u> 6.82	<u>5.55</u> 5.57	C ₁₇ H ₁₇ NO	3259	1636	980, 780	1542, 1583, 1597
11	E	190-191	<u>84.01</u> 83.49	<u>5.58</u> 5.53	<u>5.22</u> 5.12	C ₁₉ H ₁₅ NO	3289	1640	970	1560, 1588. 1600
	Ζ	68-69	<u>82,99</u> 83,49	<u>5.87</u> 5.53	<u>5.30</u> 5.12		3286 w	1639	756	1558, 1582, 1598
12	E	128-129	<u>83.90</u> 84.06	<u>8.01</u> 7.87	<u>3.65</u> 3.77	C ₂₆ H ₂₉ NO	3293	1649	974	1559, 1585. 1600
	Ζ	Viscous oil	<u>83.97</u> 84.06	<u>8.27</u> 7.87	<u>3.76</u> 3.77		3278 w	1638	755	1596, 1578, 1532
136	Z/E (1 : 2) Z/E (3 : 1)	134—140 118121	<u>65.42</u> 65.00	<u>4.34</u> 4.46	<u>7.01</u> 6.89	C ₁₁ H ₉ NOS	3231	1637	977, 755	1513, 1542, 1568
14 ^è	$\frac{Z/E}{(1:5)}$	152.4	<u>70.77</u> 70.01	<u>5.94</u> 5.88	<u>5.33</u> 5.44	C ₁₅ H ₁₅ NOS	3281	1627	980, 754	1548
15 ^b	Ε	199-201	<u>73,14</u> 73,09	<u>4.53</u> 4.69	<u>4.89</u> 5.01	C ₁₇ H ₁₃ NOS	3318	1626	964	1558

Table 1. Physicochemical properties of 2-(2-acylvinyl)pyrroles

^a In CCl₁ ($C = 1 \cdot 10^{-4} \text{ mol } L^{-1}$).

^b For compounds 13, 14, and 15: found, S(%) 15.26, 13.05, and 11.57; calculated, 15.77, 12.46, and 11.48, respectively.

Previously,³ we suggested that the initial stage of the reaction under study involves one-electron transfer to form an ion-radical pair. To verify the mechanism of the reactions of pyrroles with acylacetylenes, we studied this process further by ESR spectroscopy. However, we failed to detect the ion-radical pair under normal conditions (room temperature, benzene as the solvent). Hence, we attempted to study this reaction using the spin-capture technique. It should be noted that a signal consisting of three lines with equal intensities appeared with time in the ESR spectrum of a solution of benzoylacetylene and a spin trap, viz., 2-methyl-2-nitrosopropane (MNP), in benzene ($C = 1 \cdot 10^{-2} \text{ mol } L^{-1}$). This signal unambiguously corresponds to a spin adduct, viz., to di-tert-butyl nitroxide ($a_N = 1.580$ mT). The latter is a product of capture of a tert-butyl radical, which is formed upon decomposition of the trap as such, by the spin trap. Three spin adducts were detected in the reaction of pyrrole 1 with acetylene 6 in benzene in the presence of MNP. Initially, a triplet of di-tert-butyl nitroxide (Fig. 1, curve 1) appeared in the spectrum and then the second signal, viz., a triplet of doublets, was observed, which was attributed to interactions of the unpaired electron with one N nucleus ($a_N = 1.490 \text{ mT}$) and one proton ($a_H = 0.330 \text{ mT}$) with g = 2.0061 (Fig. 1, curve 2; the lines of the second signal are marked with circles; curve 4 represents its simulated spectrum). The intensities of the above-mentioned signals increased in the course of the reaction. After approximately 30 min, the third signal ($a_N = 1.489 \text{ mT}$; Fig. 1, curve 3; the lines are marked with crosses) was observed. The ratio of the intensities of the signals changed in the course of the reaction, which made it possible to notice that the latter signal was additionally split into six lines with equal intensities located at distances of 0.090 mT. Consequently, the unpaired electron of the nitroxide interacts with one more N atom and one proton. Its simulated spectrum is shown in Fig. 1 (curve 5). Unfortunately, it is impossible to choose between the two sets of constants of the hyperfine structure, which identically describe the observed additional splitting into six components: (1) $a_N = 0.180$ and $a_H = 0.090$ mT; (2) $a_H = 0.270$ and $a_N = 0.090$ mT.

Based on the analysis of the ESR spectra of the spin adducts, it can be suggested that ion-radical pair A formed in the reaction under study is not a stable intermediate species in a nonpolar medium. Proton transfer from the radical cation of pyrrole to the radical anion of benzoylacetylene occurred directly in the solvent "cage" (Scheme 1). Free radicals formed in this case were captured by MNP. Therefore, a triplet of doublets (marked with circles in Fig. 1) may be associated with the presence of nitroxide **B** formed as a result of successive addition of two MNP molecules to the benzoylacetylene radical. This is consistent with the published results of studies of spin adducts, *viz.*, vinyl nitroxides, by ESR spectroscopy.⁴⁻⁶ The above-mentioned constants of the hyperfine structure, which are typical of the adducts of MNP with the C



0.444 mT

ROC 'HCOR" radicals studied previously,⁷ correspond to spin adduct **B** (see Scheme 1).

If C-radical C is captured, the ESR spectrum should have a large doublet constant of splitting on the proton of the CH group. Analysis of the constants allowed the assignment of structure E to the spin adduct formed upon capture of radical D by the trap (see Scheme 1).

The experimental data obtained in the present work confirm the presence of a one-electron route in the reaction under study, though the question of whether this process forms a part of the major direction or it belongs to secondary processes remains open.

When monitoring the course of the reaction of pyrroles with acylacetylenes by TLC, we found that the process was accelerated by almost an order of magnitude in the presence of silica gel with retention of regioselectivity. Thus conversion of pyrrole 1 in the reaction with acetylene 6 without a solvent in the absence of a sorbent Scheme 1



was completed in 4 h, the reaction time in the presence of a solvent was increased to 24-48 h, while the reaction on dry silica gel was completed in 0.5 h. It is well known that SiO₂ has an activating action on the course of many reactions.⁸ However, examples of nucleophilic addition at the triple bond of acylacetylenes are absent.

It should be noted that the reaction on the SiO_2 surface afforded virtually pure *E*-isomers of compounds **8–15**, apparently due to specific sorption of acetylenes through polar and weakly basic carbonyl groups on the SiO₂ surface.

This is consistent with the fact that isomerization with the use of silica gel which has been pretreated with an aqueous solution of sodium carbonate or potassium hydroxide and dried to a constant weight occurred more slowly. Thus the reaction of pyrrole 1 with acetylene 6 on a silica gel surface pretreated with a 10% aqueous solution of Na₂CO₃ afforded both isomers of compound 8, which were isolated by elution with hexane. The reaction did not take place on a wet sorbent, in which weakly acidic coordination vacancies are occupied by water molecules.

In most cases, 2-(2-acylvinyl)pyrroles 8-15 are colored crystalline products readily soluble in organic solvents. The melting points of the *E*-isomers are substantially higher than those of the corresponding *Z*-isomers.

The structures of adducts 8-15 were established by a combination of analytical and spectral methods (Tables

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1 and 2). Their IR spectra have intense absorption bands of carbonyl groups in the 1626-1650 cm⁻¹ region. The shift of the absorption band of the carbonyl group to the short-wavelength region is due to conjugation with the double bond, which agrees with the published data.^{9,10} For the *E*-isomers, the C=C vibrations of the double bond and of the benzene and pyrrole rings¹⁰ are observed as a triplet of bands with equal intensities in the 1540-1600 cm⁻¹ region, while for the Z-isomers, the intensities of the triplet are redistributed, the lower-frequency band (1541-1546 cm⁻¹) being more intense. The spectra of compounds 13-15, containing the thiophene ring, have only one intense band $(1548 - 1558 \text{ cm}^{-1})$ in the above-mentioned region. It should be noted that the intensity of the v(C=C) band in the spectrum of an olefin is always higher than that of v(C=O), which is an indication of the s-cis-arrangement of the corresponding bonds.¹¹ In the spectra of compounds 8-15, the out-ofplane =C-H deformation vibrations of the double bond are observed in the 755–787 cm⁻¹ (for the Z-adducts) and 964–980 cm⁻¹ (for the *E*-adducts) regions.

The IR spectra of the *E*-isomers of compounds 8-15 recorded in the solid phase (KBr) have intense bands in the

3230–3320 cm⁻¹ region corresponding to N–H stretching vibrations. The spectra of solutions of the *E*-isomers of compounds **8**, **10**, and **11** in CCl₄ have only one narrow absorption band in the 3470-3480 cm⁻¹ region, which is indicative of the presence of a free NH group.

A different situation is observed in the case of the Z-isomers of compounds 8 and 11. The spectra of solutions in CCl_4 at concentrations which completely exclude intermolecular hydrogen bonding have a broad band with two maxima at 3150-3180 cm⁻¹, which is attributable to intramolecular hydrogen bonding in the structures (F):



Table 2.	^I H NMR	spectral of	data for	the	E- and	Z-isomers	of	2-(2-acy	vlvinyl)pyrrole	es
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Com- pound	Isomer	····	$^{3}J_{\mu}/Hz$						
		N-H	H(3)	RI	R ²	H-orthoa (CO-Ph)	H	Η _β	u,p
8	E	11.75	6.75	7.15	6.24	8.05	7.58	7.64	15.40
	Ζ	12.82	6.83	7.28	6.34	8.05	6.81	7.08	12.30
9	Ε	8.90	6.54	1.20 - 2.80	2.30	7.95	7.02	7.66	15.53
	Z	13.00	6.50	1.20-2.80	2.30	7.95	6.47	6.79	12.18
10	Ε	8.27	6.43	1.70 - 1.90	2.50-2.62	7.95	6.96	7.63	15.53
	Ζ	12.85	6.40	1.70-1.90	2.54-2.72	7.95	6.48	6.80	12.18
11	Ε	11.78	6.95	7.25-7.80	6.98	8.15	7.53	7.68	15.30
	Z	13.72	6.74	7.25-7.80	6.86	8.05	6.90	7.13	12.30
12	E	9.36	6.69	7.28-7.95	1.25; 2.68	7.93	7.17	7.83	15.50
	Z	13.44	6.60	7.28-7.95	1.60; 2.68	7.67	6.61	6.88	12.30
13 ^b	E	8.85	6.69	6.97	6.31		7.00	7.74	15.53
	Z	12.98	6.63	7.04	6.32		6.52	6.87	12.33
14 ^b	E	8.45	6.46	1.70-1.90	2.49; 2.63		6.87	7.70	15.23
	Ζ	12.72	6.37	1.70-1.90	2.52; 2.69		6.38	6.76	12.00
15 ^{b,c}	E	11.76	6.85	7.28-7.80	6.68		7.53	7.71	15.30

^a The signals for the *meta*- and *para*-protons of the benzene rings form complex multiplets at δ 7.40–7.50.

^b The signals for the H(3, 4, 5) protons of the thiophene ring are observed at δ 7.60, 7.12, and 7.77 (*E*-isomer of 13); 7.71, 7.14, and 7.94 (*Z*-isomer of 13); 7.75, 7.11, and 7.57 (*E*-isomer of 14); 7.71, 7.11, and 7.57 (*Z*-isomer of 14); 7.85, 7.25, and 8.02 (*E*-isomer of 15), respectively.

^c In DMSO.

Table 3. Geometric parameters of the calculated forms of compound 8 and the difference in their total energies

Struc-			Bond I	$\theta_{\rm Ph}/deg$	∆ <i>E</i> */kJ_mol ^{−1}					
ture	C≠0	C=C	N-H	C(1)-C(2)	C(3)-C(4)	C(1) - C(5)				
F	1.209	1.344	0.998	1.471	1.442	1.502	25.5	0.00		
G	1.201	1.339	0.993	1.478	1.450	1.504	24.1	32.79		
н	1.202	1.331	0.994	1.484	1.451	1.502	20.1	11.72		
I	1.201	1.333	0.992	1.483	1.447	1.502	22.2	9.11		

* The values are given relative to the most stable form (F).

Structure **F** as well as other most probable structures (G-I) were calculated by the *ab initio* quantum-chemical method with the 6-31G* basis set, polarization functions, and full geometry optimization (Table 3).



The distance between the H atom of the NH group and the O atom of the carbonyl group (1.896 Å) and the changes in the bond lengths in structure F (elongation of the C=O, N-H, and C=C bonds and shortening of the C(1)-C(2) and C(3)-C(4) bonds) compared to the bond lengths in structures G-I (see Table 3) confirm the presence of a strong intramolecular hydrogen bond in conformation F.

In all the structures calculated, the carbonyl group lies virtually in the plane of the heterocycle and the C=C bond. The phenyl ring is bent away from the plane of the C=C bond (the angles of rotation are $20-26^{\circ}$), which leads to weakening of the conjugation between the phenyl fragment and the π -system of the double bonds. This fact is confirmed by the data of UV spectroscopy. Thus the following electron-transition bands are observed in the spectrum of a solution of compound 8 in MeCN $(\lambda/nm (log_{\epsilon}))$: 257 (3.94) and 382 (4.30) for the Z-isomer and 257 (3.94) and 367 (4.37) for the E-isomer. The first electron transition is virtually completely localized on the phenyl fragment. The longwavelength intense band is indicative of transfer of the electron density from the C=C $-\pi$ -system fragment of the pyrrole ring to the O atom of the carbonyl group and belongs to charge-transfer bands.

In the ¹H NMR spectra of compounds 8–12 (see Table 2), the signals for the *ortho*-protons of the benzene ring are shifted downfield under the effect of the adjacent carbonyl group and are far removed from the signals for the *meta*- and *para*-protons, which form complex multiplets in the δ 7.4–7.5 region. In compounds 13–15, the signals for the protons of the thiophene fragment are observed at δ 7.1–7.7 and the spin-spin coupling constants have standard values (${}^{3}J_{H(4'),H(3')} = 3.8$ Hz, ${}^{3}J_{H(2'),H(3')} = 4.9$ Hz, ${}^{4}J_{H(4'),H(2')} = 1.1$ Hz).

The multiplicity of the signals for the protons of the pyrrole ring is complicated by the effect of the proton of the NH group, which is typical of all the compounds **8–15**. Thus the long-range spin-spin coupling constant ${}^{4}J_{\rm NH,H(3)}$ for compounds **10** and **14** is 2.05 Hz.

From Table 2 it can be seen that the chemical shifts of the olefinic protons of the Z-isomers are always smaller than those of the E-isomers. Noteworthy also are the unusually high values of the ${}^{3}J_{AB}$ constants for the Z-isomers (12.18-12.33 Hz), which is untypical of the constants of vicinal interactions through double bonds, though analogous values are available in the literature.^{12,13} In the case under consideration, this value was confirmed by the double resonance method. The signal for the proton of the NH group (δ 12.72–13.72) of the Z-isomers is shifted downfield compared to that of the E-isomers (δ 8.45-11.72), which is due to the formation of an intramolecular hydrogen bond between the proton of the NH group and the O atom of the carbonyl group. The twodimensional ¹H NMR spectra recorded with the use of the nuclear Overhauser effect unambiguously confirm the assignment of the signals for the H_{α} and H_{β} protons at the double bond of the *E*- and *Z*-isomers. For adduct $\mathbf{8}$, it was demonstrated that both isomers are in the s-cis-conformation with respect to the mutual arrangement of the double bond and the carbonyl group. Thus in the case of the E-isomer, the high-field doublet corresponding to the H_α proton has a cross-peak with the proton of the NH group and with the ortho-protons of the benzene ring, while a low-field doublet of the H_B proton has a cross-peak only with H(3). For the Z-isomer, the signal for the H_{α} proton is characterized by cross-peaks with the signals for the H_{B} proton and for the ortho-protons of the benzene ring (the mixing period (0.9 s) was close to the relaxation time). Therefore, the E- and Z-isomers exist in different rotameric forms. In the E-isomer, the carbonyl group is in the anti-position with respect to the N atom (anti-s-cis-rotamer, structure I), while in the Z-isomer, these fragments are in close proximity (syns-cis-rotamer, structure \mathbf{F}), which confirms the presence of an intramolecular hydrogen bond in the latter.

Experimental

The IR spectra of the compounds synthesized were recorded on a Bruker IFS-25 Fourier spectrometer in the 400–4000 cm⁻¹ region in KBr pellets and in CCl₄ solutions (the concentration was $1 \cdot 10^{-3} - 1 \cdot 10^{-4}$ mol L⁻¹; the thickness of the layer was $5 \cdot 10^{-2} - 1 \cdot 10^{-1}$ m). The ¹H NMR spectra were measured on a Bruker DPX 250 instrument (250.13 MHz) with HMDS as the internal standard; CDCl₃ was used as the solvent. The UV spectra were obtained on a Specord UV–VIS instrument. The ESR spectra were recorded on an SE/X-2547 Radiopan spectrometer (Poland).

The course of the reactions and the purities of the resulting compounds were monitored by TLC on Silufol UV-254 plates in 1:1 ether—hexane and 1:1 ether—light petroleum systems.

Preparative separation of isomers and purification were carried out by TLC and column chromatography on Al_2O_3 using light petroleum and diethyl ether as the eluents.

Pyrrole 1 was a commercial product. Pyrroles 2-5 were prepared according to Trofimov's reaction.¹⁴

2-(2-Acylvinyl)pyrroles 8-15. Method A. A mixture of pyrrole 1 (0.134 g, 2 mmol) and benzoylacetylene 6 (0.260 g, 2 mmol) was kept at ~20 °C for 4 h. The reaction mixture that turned crystalline was washed with EtOH and ether. A mixture of 2-(Z/E-2-benzoylvinyl)pyrroles (8) (Z/E = 1 : 2) was obtained in a yield of 0.284 g (72%).

A mixture of 2-(Z/E-2-benzoylvinyl)-5-isopropyl-4-methylpyrroles (9) was prepared analogously from pyrrole 2 (0.123 g, 1 mmol) and benzoylacetylene 6 (0.130 g, 1 mmol) (the reaction time was 4 h). A mixture of pyrroles 9 (Z/E =1 : 5) was isolated by column chromatography in a yield of 0.149 g (59%).

A mixture of 2-(Z/E-2-benzoylvinyl)-4,5,6,7-tetrahydroindoles (10) (<math>Z/E = 1 : 5) was prepared analogously from tetrahydroindole 3 (0.121 g, 1 mmol) and acetylene 6 (0.130 g, 1 mmol) in a yield of 0.136 g (54%) (the reaction time was 1 h).

Method B. A mixture of pyrrole 1 (0.140 g, 2.1 mmol) and acetylene 6 (0.260 g, 2 mmol) in anhydrous EtOH (2 mL) was stirred for 30 min and kept at ~20 °C for 24 h. After removal of the solvent, a mixture of isomers of compound 8 (Z/E = 1 : 1.6) was isolated by column chromatography in a yield of 0.23 g (58%).

Two fractions of Z/E isomers of 2-(2-thenoylvinyl)pyrroles (13) were obtained analogously from pyrrole 1 (0.067 g, 1 mmol) and acetylene 7 (0.134 g, 1 mmol) in ether (2 mL) (the reaction time was 24 h). The fractions were obtained in yields of 0.076 g (37%) (Z/E = 1 : 2) and 0.05 g (24%) (Z/E = 1.2 : 1).

 $2 \cdot (Z/E-2$ -Thenoylvinyl)-4,5,6,7-tetrahydroindoles (14) (Z/E = 1 : 5) were prepared analogously from tetrahydroindole 3 (0.121 g, 1 mmol) and acetylene 7 (0.134 g, 1 mmol) in ether (2 mL) (the reaction time was 24 h) in a yield of 0.225 g (87%).

2-(*E*-2-Thenoylvinyl)-5-phenylpyrrole (15) (the admixture of the *Z*-isomer was 5%) was obtained analogously from pyrrole 4 (0.143 g, 1 mmol) and acetylene 7 (0.134 g, 1 mmol) in ether (2 mL) (the reaction time was 24 h) in a yield of 0.238 g (85%).

Method C. Acetylene **6** (0.260 g. 2 mmol) was added to a mixture of pyrrole **1** (0.134 g, 2 mmol) and SiO₂ (4 g) at ~20 °C. The reaction mixture turned bright-yellow and slightly warmed up (30–31 °C). After 30 min, the reaction mixture was extracted with hexane. Adducts **8** (Z/E = 1 : 9, ¹H NMR) were obtained in a yield of 0.290 g (74%). Compound *E*-**8** was isolated by column chromatography, m.p. 133–134 °C (lit. data¹⁵: m.p. 134 °C).

2-(*E*-2-Benzoylvinyl)-5-phenylpyrrole (11) was prepared analogously from pyrrole 4 (0.143 g, 1 mmol) and acetylene 6 (0.130 g, 1 mmol) (the reaction time was 30 min) in a yield of 0.180 g (66%).

Method D. Acetylene 6 (0.130 g, 1 mmol) was added to a mixture of pyrrole 1 (0.067 g, 1 mmol) and dry SiO₂ (2 g) pretreated with a 10% aqueous solution of Na₂CO₃. The reaction mixture turned yellow. After 30 min, lemon-yellow crystals of adduct Z-8 were isolated by extraction with hexane in a yield of 0.110 g (56%). Subsequent treatment of the reaction mixture with a 1 : 1 mixture of diethyl ether and

hexane afforded E-8 isomer as orange-yellow crystals in a yield of 0.025 g (13%).

The Z- and E-isomers of 2-(2-benzoylvinyl)-4-heptyl-5phenylpyrrole (12) were prepared analogously from pyrrole 5 (0.241 g, 1 mmol) and acetylene 6 (0.130 g, 1 mmol) on silica gel pretreated with a 10% aqueous solution of KOH (the reaction time was 20 min) in yields of 0.250 g (68%) and 0.08 g (22%), respectively.

The Z-isomer (the admixture of the E-isomer was 6%) and the E-isomer of adduct 11 were prepared analogously from pyrrole 4 (0.143 g, 1 mmol) and acetylene 6 (0.130 g, 1 mmol) (the reaction time was 30 min) in yields of 0.031 g (11%) and 0.112 g (41%), respectively.

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