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B.A.Trofimov on Occasion of His 65th Birthday

Synthesis and X-Ray Diffraction Study of 2-(2-Acyl-1-phenylethenyl)pyrroles

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Received January 8, 2003

Abstract—Pyrroles add to 2-acyl-1-phenylacetylenes on the surface of silicon dioxide at 20–90°C affording structurally stable Z-isomers of 2-(2-acyl-1-phenylethenyl)pyrroles containing a strong intramolecular hydrogen bond. The geometry of these molecules was established by X-ray diffraction analysis of a single crystal of 2-(2-benzoyl-1-phenylethenyl)-4,5,6,7-tetrahydroindole.

Pyrroles react with terminal acylacetylenes under mild conditions (at room temperature) both in a solvent and without it affording a mixture of *E/Z*-2-(2-acylethenyl)pyrroles [1–3]. According to preliminary data published without experimental details [4] the reaction between 2-phenylpyrrole and 2-acyl-1-phenylacetylene required more stringent conditions (prolonged heating or heating on the surface of silicon dioxide) and furnished exclusively configurationally stable *Z*-2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles.

To get further insight into specific features of this reaction and also with a goal to extend the series of 2-(2-acyl-1-phenylethenyl)pyrroles as promising building blocks in designing new heterocyclic compounds we investigated the reaction between pyrroles **I–III** and 2-acyl-1-phenylacetylenes **IV–VIII** proceeding on the silicon dioxide.

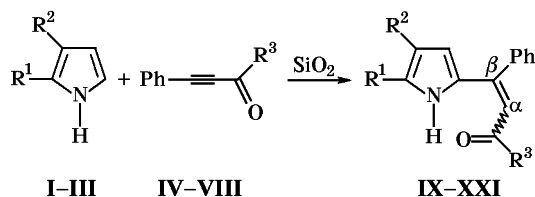
We established that pyrroles **I–III** added to acetylenes **IV–VIII** at 20–90°C, affording predominantly

(with pyrrole **I**) or exclusively (with pyrroles **II** and **III**) *Z*-2-(2-acyl-1-phenylethenyl)pyrroles **IX–XXI** in 13–90% yield.

The ethenylation of pyrroles **I–III** with acetylenes **IV–VIII** depended essentially on the structure of initial reagents (Table 1). As shown before [4], 2-phenylpyrrole (**III**) heated to 85–90°C with acetylenes **IV–VI** on the silicon dioxide surface formed in a high yield *Z*-2-(2-acyl-1-phenylethenyl)pyrroles **XVII–XIX** containing a strong intramolecular hydrogen bond whose presence was confirmed by X-ray diffraction analysis [5].

Under similar conditions pyrrole (**I**) reacted with acetylenes **IV, V** to yield polymeric powders of intractable structure, and only with acetylene **VI** adduct **XI** was obtained in 43% yield. 2-(2-Acyl-1-phenylethenyl)pyrroles **IX, X** were isolated in a low yield (19–20%) when the reaction temperature was decreased to 75–80°C.

The highest activity in the reaction with acylacetylenes showed 4,5,6,7-tetrahydroindole (**II**): its reaction with acetylene **IV** on silicon dioxide even at room temperature within 4 h afforded adduct **XII** in 46% yield. Without silicon dioxide a comparable yield of adduct **XII** (56%) was obtained in 12 h. For reference: pyrrole **III** added to acetylene **IV** on silicon dioxide within 20 h at room temperature furnishing adduct **XVII** in 28% yield. Under these conditions the reaction did not occur without silicon dioxide. Under more stringent conditions (10 h, 85–90°C) pyrrole **XVII** was obtained from compounds **III** and **IV**, but the yield did not exceed 29%.



R¹ = H (**I, IX–XI**), Ph (**III, XVII–XXI**); R² = H (**I, III, IX–XI, XVII–XXI**), R¹, R² = (CH₂)₄ (**II, XII–XVI**); R³ = Ph (**IV, IX, XII, XVII**), 2-furyl (**V, X, XIII, XVIII**), 2-thienyl (**VI, XI, XIV, XIX**), Et (**VII, XV, XX**), CCl₃ (**VIII, XVI, XXI**).

At the same time under conditions optimum for preparation of pyrrole **XVII** (SiO_2 , 85–90°C, 2 h, 77%) pyrrole **XII** formed only in 55% yield. This fact is apparently due to instability of initial pyrrole **II** in the presence of silicon dioxide. Actually we demonstrated that within 12 h at room temperature pyrrole **II** on silicon dioxide was to 70–75% converted into tarry products which we did not studied. To increase the yield of adducts **XII–XVI** we sometimes used silicon dioxide treated with 5% solution of Na_2CO_3 .

The yield of adducts is still more sensitive to the character of the acyl radical in the acetylene substrate. For instance, we failed to isolate adducts of pyrrole **II** to acetylenes **VII** and **VIII**. The experiments performed both with silicon dioxide and without it at different temperature and duration of the process resulted in polymer powders of bright color and possessing paramagnetic properties ($N\ 1 \times 10^{18}$ spins per g, $\Delta H\ 5.8$ Oe, $g\ 2.0031$, singlet). The proton signals in the ^1H NMR spectra of the polymers are broadened. The nature of the substances is not yet identified

Under all conditions described above pyrrole **II** reacted with acetylene **VII** in the same way as pyrrole **I** affording paramagnetic powders ($N\ 3.9 \times 10^{18}$ spins per g, $\Delta H\ 6.4$ Oe, $g\ 2.0042$) with composition close to that of adducts. Evidently the latter are unstable under the reaction conditions and easily undergo polymerization. The inhibition of the polymerization with *p*-benzoquinone simultaneously decelerated the ethenylation: (1*Z*)-1-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-phenylpent-1-en-2-one (**XV**) was isolated only in a mixture with unreacted acetylene **VII**. Presumably the ethenylation of pyrroles **I–III** with internal acetylenes **IV–VIII** on the silicon dioxide proceeds as ion-radical process in the same fashion as the reaction of pyrroles with terminal acetylene we have investigated before [1, 2].

We succeeded to obtain (3*Z*)-4-phenyl-4-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1,1,1-trichlorobut-3-en-2-one (**XVI**) in 13% yield (room temperature, 20 h) only using silicon dioxide deactivated with sodium carbonate solution.

With 2-phenylpyrrole acetylenes **VII** and **VIII** reacted at room temperature affording pyrroles **XX**, **XXI** in 33 and 37% yield respectively.

As already mentioned, the reaction of pyrroles **II**, **III** with acetylenes **IV–VIII** occurred stereoselectively yielding adducts **XII–XXI** always as *Z*-isomers. And only with pyrrole **I** in some cases were detected and even isolated the *E*-isomers.

Table 1. Effect of reaction conditions and initial reagents structure on the yield of pyrroles **IX–XXI** (equimolar quantities of reagents, 10-fold amount of silicon dioxide)

Pyrrole	Acetylene	Adduct	Time of reaction, h	Temperature of reaction, °C	Yield of adduct, %
I	IV	IX	1.5	75–80	20
I	V	X	1.5	75–80	19
I	VI	XI	2	85–90	43
II	IV	XII	4	20–25	46
II ^a	IV	XII	12	20–25	53
II ^b	IV	XII	1.5	75–80	74
II	IV	XII	2	85–90	55
II ^b	V	XIII	1.5	75–80	90
II ^b	VI	XIV	1.5	75–80	89
II ^c	VII	XV	2	20–25	34 ^d
II ^b	VIII	XVI	20	20–25	13
III ^a	IV	XVII	10	85–90	29
III	IV	XVII	20	20–25	28
III	IV	XVII	2	85–90	77
III	V	XVIII	2	85–90	87
III	VI	XIX	2	85–90	89
III	VII	XX	70	20–25	33
III ^e	VIII	XXI	1.5	20–25	37

^a Without SiO_2 .

^b SiO_2 deactivated with 5% Na_2CO_3 solution.

^c In the presence of *p*-quinone.

^d In a mixture with acetylene **VII**.

^e The synthesis is described in [6].

For instance, adduct **IX** formed as a mixture of *E*- and *Z*-isomers (75–80°C, 1.5 h). Under the same conditions acetylene **V** furnished only *Z*-isomer of compound **X**. The *E*-isomer in 5% yield was obtained at lower temperature (60–65°C).

Thus in this case the *E*-isomer is a kinetic product which at further heating and during workup or just at standing in solution transforms into the more stable *Z*-isomer. The high stability of the latter is evidently caused by formation of an intramolecular hydrogen bond $\text{N-H}\cdots\text{O}=\text{C}$.

The involvement of the N–H bond into a strong intramolecular interaction is revealed in spectral characteristics of compounds synthesized: the chemical shift of NH protons in the ^1H NMR spectra of adducts **IX–XXI** is $\delta\ 13.00\text{--}14.00$ ppm, the frequency of the stretching vibrations $\nu(\text{NH})$ is $\sim 3000\ \text{cm}^{-1}$ (determined in [6] for adduct **XXI**), the

Table 2. Geometrical parameters in a crystal of a molecule of (2*Z*)-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1,3-diphenylprop-2-en-1-one (**XII**) (numbering of atoms as on figure)

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
O ¹ -C ¹¹	1.245 (2)	C ¹ -C ⁶	1.390 (3)
C ⁸ -C ⁹	1.429 (3)	C ⁶ -C ⁷	1.395 (3)
C ⁹ -C ¹⁰	1.373 (3)	C ⁷ -C ⁸	1.403 (3)
C ¹⁰ -C ¹¹	1.448 (3)	C ¹ -C ²	1.488 (3)
N ¹ -C ⁸	1.381 (2)	C ⁹ -C ¹⁸	1.503 (3)
N ¹ -C ¹	1.349 (2)	C ¹¹ -C ¹²	1.501 (3)
Bond angle	ω, deg	Torsion angle	τ, deg
H(N ¹)N ¹ C ¹	128.0 (13)	N ¹ C ¹ C ² C ³	-168.5 (2)
H(N ¹)N ¹ C ⁸	121.9 (13)	N ¹ C ⁸ C ⁹ C ¹⁰	-1.9 (3)
N ¹ C ⁸ C ⁹	123.5 (2)	O ¹ C ¹¹ C ¹⁰ C ⁹	4.9 (4)
C ⁸ C ⁹ C ¹⁰	130.2 (2)	C ¹⁰ C ¹¹ C ¹² C ¹³	29.3 (3)
C ⁹ C ¹⁰ C ¹¹	132.6 (2)	C ⁸ C ⁹ C ¹⁸ C ¹⁹	61.3 (2)
O ¹ C ¹¹ C ¹⁰	125.5 (2)	C ¹⁰ C ⁹ C ¹⁸ C ¹⁹	-118.9 (2)
O ¹ C ¹¹ C ¹²	117.3 (2)	C ¹⁰ C ¹¹ C ¹² C ¹⁷	-152.0 (2)
		O ¹ C ¹¹ C ¹² C ¹⁷	26.7 (3)

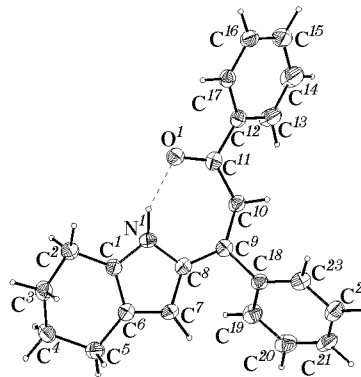
Table 3. Parameters of H-bonds in (2*Z*)-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1,3-diphenylprop-2-en-1-one (**XII**) and (2*Z*)-1,3-diphenyl-3-(5-phenyl-1*H*-pyrrol-2-yl)prop-2-en-1-one (**XVII**)

Bond	<i>D</i>	
	(XII)	(XVII)
N ¹ -H ¹	0.91 (2)	0.99 (2)
H ¹ ...O ¹	1.80 (2)	1.70 (2)
N ¹ ...O ¹	2.640 (2)	2.620 (2)
N ¹ H(N ¹)...O ^{1a}	152 (2)	153 (2)

^a Angle, deg.

absorption band of carbonyl group stretching vibrations is shifted to the low-frequency region (ν 1600–1614 cm⁻¹) in the IR spectra of adducts recorded in the solid phase (KBr pellets).

The presence of a strong intramolecular hydrogen bond in the compounds under investigation was previously confirmed by X-ray diffraction analysis and quantum-chemical calculations for pyrroles **XVII** and **XVIII**. It was shown that in the crystalline state the central fragment of the molecule formed a 7-membered ring closed by a strong intramolecular hydrogen bond NH...O [5].



Molecular structure and numbering of atoms of (2*Z*)-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1,3-diphenylprop-2-en-1-one (**XII**). Nonhydrogen atoms are represented as their 50% parameters of anisotropic displacement.

Here we report on the results of the X-ray diffraction analysis of a single crystal of (2*Z*)-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1,3-diphenylprop-2-en-1-one (**XII**). The bond lengths, bond and torsion angles of some fragments of the molecule are compiled in Table 1, and parameters of H-bonds in Table 3. The general view of the molecule is presented on figure.

In a crystal the molecule of pyrrole **XII** has *Z*-form with *s-cis* position of carbonyl group and olefin bond C=C. Similar structure was established for compounds **IX–XXI** in CDCl₃ solution by recording the ¹H NMR spectra with the Overhauser effect.

The results of X-ray diffraction study of pyrrole **XII** show the increased length of the C=O bond [1.245(2) Å] as compared to that characteristic of a free carbonyl bond in a fragment C=C-C=O (1.208 Å) [7]. The C=C bond in molecule **XII** also gets longer [1.373(3) instead of 1.325 Å], and the =C-C= bond is on the other hand shortened from 1.486 to 1.448(3) Å. These changes in the lengths of bonds observed also in the molecules of compounds **XVII**, **XVIII** may be ascribed to the delocalization of electron density along the 7-membered ring intensified by the formation of hydrogen bond N-H...O [8]. The observed high degree of delocalization evidently suggests that the N-H...O bond in compound **XII** is strong. The comparison of hydrogen bond N-H...O parameters in compounds **XII** and **XVII** (Table 3) indicates that it is slightly less strong in compound **XII** probably due to the presence of a cycloalkyl substituent in the molecule. Still the distance N¹...O¹ [2.640(2) Å] remains notably shortened compared to N...O in common internal hydrogen bonds (the length of N...O is

2.9–3.2 Å [9]) demonstrating the high strength of the hydrogen bond in compound **XII**.

Thus the complex of our experimental data evidences that in compound **XII** formed a strong intramolecular hydrogen bond N–H...O that apparently was the main cause governing the spatial structure of 2-(2-acyl-1-phenylethenyl)pyrroles.

EXPERIMENTAL

IR spectra of compounds synthesized in KBr pellets were recorded on spectrometer JFS-25, UV spectra were run on spectrophotometer Specord UV-Vis in acetonitrile. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-250 at operating frequencies 250.13 and 62.9 MHz respectively from chloroform solutions, internal reference HMDS. In recording two-dimensional spectra NOESY a standard procedure was applied with the mixing period of 1.2 s [10, 11]. Analyses of the reaction mixture and checking of compounds purity was performed by TLC on Silufol UV-254 plates, eluent hexane–ethyl ether, 1:1, 2:1. Preparative separation of compounds obtained was carried out by column chromatography on Al_2O_3 .

Pyrrol (**I**) used was a commercial product, 4,5,6,7-tetrahydroindole (**II**) and 2-phenylpyrrole (**III**) were prepared by Trofimov reaction [12]. Silicon dioxide (silica gel, L 100/160 μ , pH 6–7, Chemapol) was washed with distilled water or with 5% solution of Na_2CO_3 and water, and dried till constant weight.

X-ray diffraction study of compound XII. The experiment was carried out at 150 K on prismatic crystal of the habit $0.6 \times 0.2 \times 0.2$ mm. The sample temperature was maintained by the low-temperature device LT-2. The cell parameters and crystal structure of compound **XII** were measured on automatic diffractometer Syntex P2₁ (50 kV and 20 mA), $\lambda(\text{MoK}\alpha)$ 0.71073 Å. Crystals of pyrrole **XII** monoclinic, a 11.925 (3), b 6.224 (2), c 23.133 (6) Å, β 92.55 (2)°, V 1715.3 (8) Å³, space group $P2(1)/c$, Z 4, ρ_{calc} 1.268 g cm⁻³, μ 0.077 mm⁻¹. The values of integral intensities of 3761 independent reflections (R_{int} 0.022) with accounting for Lorentz correction and for polarization were obtained with the use of PROFIT software [13]; the absorption was not taken in consideration.

The structure was solved by the direct method and refined in full-matrix least-squares procedure along F^2 applying the software package SHELXTL PLUS [14]. All nonhydrogen atoms were refined in anisotropic approximation, the hydrogen atoms were re-

vealed from the difference Fourier synthesis and were refined in isotropic approximation. The overall number of refined parameters 310. The final divergence factors R_1 0.0628 [calculated by F for 2192 reflections with $I > 2\sigma(I)$], wR_2 0.1245 (calculated by F^2 for all 3761 reflections taken into account at the last stage of refinement). G_{ooF} 1.034.

(2*E*,*Z*)-3-(1*H*-Pyrrol-2-yl)-1,3-diphenylprop-2-en-1-one (**IX**).

A mixture of 0.067 g (1 mmol) of pyrrole (**I**), 0.206 g (1 mmol) of acetylene **IV**, and 2.8 g of silicon dioxide was heated at 75–80°C for 1.5 h. The red-orange reaction mixture was washed with hexane and then with ethanol. After partial evaporation of hexane at room temperature from the lemon-yellow hexane solution were separated 0.008 g (3%) of green-yellow fine needle crystals of the *E*-isomer of adduct **IX**, mp 127–127.5°C. On complete evaporation of hexane the 0.047 g (17%) of residue contained *E*- and *Z*-isomers of adduct **IX**, mp 121–123°C (*E* to *Z*, 4:1). The orange-red ethanol solution was evaporated, the residue was ground with hexane, the precipitate was filtered off, and washed with hexane–ether mixture, 3:1. We obtained 0.132 g (48 wt% with respect to reagents taken) of brick-red powder, mp 128–126°C. In the ^1H NMR spectrum of the latter appear broadened signals of protons in the region 6.0–8.5 ppm, and the NH group proton signal at 14.0 ppm. IR spectrum of *E*-isomer, ν , cm⁻¹: 603, 619, 647, 700, 719, 763, 779, 846, 883, 910, 975, 998, 1024, 1038, 1075, 1088, 1137, 1178, 1208, 1236, 1292, 1313, 1358, 1391, 1429, 1451, 1489, 1507, 1522, 1538, 1576, 1595, 1625, 1640, 2924, 2965, 3058, 3102, 3198, 3246. ^1H NMR spectrum of *E*-isomer, δ , ppm: 6.33 m (1H, H⁴), 6.61 m (1H, H³), 6.92 m (1H, H⁵), 7.19 s (1H, CH=), 7.30 m (1H, H_{*p*}, Ph), 7.35 m (2H, H_{*m*}, Ph), 7.40 m (2H, H_{*o*}, Ph), 7.46 m (2H, H_{*m*}, COPh), 7.49 m (1H, H_{*p*}, COPh), 7.90 m (2H, H_{*o*}, COPh), 8.30 br.s (1H, NH). ^{13}C NMR spectrum, δ , ppm: 111.20 (C³), 112.42 (C⁴), 115.60 (C ^{α}), 122.14 (C⁵), 128.40 (C_{*o*}, Ph), 128.40 (C_{*m*}, COPh), 128.40 (C_{*o*}, COPh), 128.54 (C_{*p*}, Ph), 129.13 (C_{*m*}, Ph), 132.27 (C_{*p*}, COPh), 132.64 (C²), 137.70 (C_{*i*}, Ph), 139.36 (C_{*i*}, COPh), 147.32 (C ^{β}), 190.60 (C=O). ^1H NMR spectrum of *Z*-isomer, δ , ppm: 6.27 m (1H, H³), 6.34 m (1H, H⁴), 6.68 s (1H, CH=), 7.19 m (1H, H⁵), 7.30 m (1H, H_{*p*}, Ph), 7.35 m (2H, H_{*m*}, Ph), 7.40 m (2H, H_{*o*}, Ph), 7.45 m (2H, H_{*m*}, COPh), 7.50 m (1H, H_{*p*}, COPh), 8.02 m (2H, H_{*o*}, COPh), 14.04 br.s (1H, NH). ^{13}C NMR spectrum, δ , ppm: 111.45 (C⁴), 114.53 (C ^{α}), 120.87 (C³), 123.85 (C⁵), 128.03 (C_{*o*}, Ph), 128.35 (C_{*o*}, COPh), 128.51 (C_{*p*}, Ph), 128.59 (C_{*m*}, COPh), 129.16 (C_{*m*}, Ph), 131.73 (C²),

132.27 (C_p , COPh), 140.45 (C_i , COPh), 143.28 (C_i , Ph), 150.67 (C^{β}), 190.05 (C=O).

(2*E,Z*)-3-(1*H*-Pyrrol-2-yl)-3-phenyl-1-(2-furyl)prop-2-en-1-one (X). (a) A mixture of 0.067 g (1 mmol) of pyrrole (I), 0.196 g (1 mmol) of acetylene V, and 2.7 g of silicon dioxide was heated at 75–80°C for 1.5 h. The red-orange reaction mixture was cooled to room temperature and washed in succession with hexane (green-yellow fraction), hexane–ether mixture, 2:1 (orange-yellow fraction), and ethanol (orange-red fraction). On removing hexane 0.018 g (7%) of lemon-yellow oily residue was obtained containing a mixture of the initial reagents and the adduct. From the hexane–ether fraction was isolated a dark-yellow solid which on recrystallization from aqueous ethanol (1:2) gave 0.049 g (19%) of orange-yellow crystalline *Z*-isomer of pyrrole X, mp 89°C. IR spectrum, ν , cm^{-1} : 585, 604, 615, 649, 706, 744, 769, 786, 798, 831, 855, 882, 898, 930, 984, 999, 1015, 1038, 1050, 1083, 1095, 1148, 1175, 1220, 1255, 1269, 1305, 1357, 1386, 1429, 1446, 1493, 1509, 1535, 1535, 1570, 1613, 2854, 2922, 3026, 3055, 3101, 3129. ^1H NMR spectrum, δ , ppm: 6.26 m (1H, H^3), 6.33 m (1H, H^4), 6.57 d.d (1H, H^4 , J 3.5, 1.6 Hz), 6.61 s (1H, CH=), 7.18 m (1H, H^5), 7.26 d.d (1H, H^3 , J 3.5, 1.0 Hz), 7.45 m (3H, $H_{m,p}$, Ph), 7.50 m (2H, H_o , Ph), 7.60 d.d (1H, H^5 , J 1.6, 1.0 Hz), 14.05 br.s (1H, NH). ^{13}C NMR spectrum, δ , ppm: 111.49 (C^4), 112.68 (C^4), 113.17 (C^{α}), 116.87 (C^3), 120.85 (C^3), 124.18 (C^5), 128.03 (C_o , Ph), 128.53 (C_p , Ph), 129.13 (C_m , Ph), 131.75 (C^2), 142.99 (C_i , Ph), 146.21 (C^5), 150.77 (C^{β}), 155.06 (C^2), 177.52 (C=O). Found, %: C 76.89; H 5.09; N 5.63. $\text{C}_{17}\text{H}_{13}\text{NO}_2$. Calculated, %: C 77.55; H 4.98; N 5.32.

The fragile cherry-red film (0.084 g) obtained on evaporating ethanol from the last fraction was ground in hexane, the precipitate was filtered off and washed with a mixture hexane–ether, 3:1. We obtained 0.062 g (23%) of cherry-red powder, mp 130–135°C (decomp.).

(b) A mixture of 0.067 g (1 mmol) of pyrrole (I), 0.196 g (1 mmol) of acetylene V, and 3.0 g of silicon dioxide was heated at 60–65°C for 2 h. Then the yellow-orange reaction mixture was rapidly washed with cold petroleum ether, the main fraction was eluted with chloroform. The residue after removing chloroform (0.234 g) was a dark-orange oily substance containing a mixture of *E*- and *Z*-isomers of pyrrole X and partly unreacted reagents. On dissolving the residue in aqueous methanol we isolated

0.013 g (5%) of *E*-isomer of pyrrole X as orange lustrous plates, mp 91–92°C (aqueous methanol 1:2). ^1H NMR spectrum, δ , ppm: 6.30 m (1H, H^4), 6.46 d.d (1H, H^4 , J 3.5, 1.6 Hz), 6.60 m (1H, H^3), 6.88 m (1H, H^5), 7.08 d.d (1H, H^3 , J 3.5, 1.0 Hz), 7.16 s (1H, CH=), 7.27 m (1H, H_p , Ph), 7.38 m (4H, $H_{o,m}$, Ph), 7.50 d.d (1H, H^5 , J 1.6, 1.0 Hz), 8.29 br.s (1H, NH). Found, %: C 77.46; H 5.16; N 5.29. $\text{C}_{17}\text{H}_{13}\text{NO}_2$. Calculated, %: C 77.55; H 4.98; N 5.32.

(2*Z*)-3-(1*H*-Pyrrol-2-yl)-1-(2-thienyl)-3-phenylprop-2-en-1-one (XI). A mixture of 0.067 g (1 mmol) of pyrrole (I), 0.212 g (1 mmol) of acetylene III, and 2.8 g of silicon dioxide was heated at 85–90°C for 2 h till the reaction mixture acquired a stable dark-orange color. The reaction mixture was washed with hexane. On evaporating the hexane the residual oily substance was ground in ethanol, and 0.120 g (43%) of bright-yellow crystals of pyrrole XI was thus separated, mp 100–101°C. IR spectrum, ν , cm^{-1} : 586, 604, 635, 667, 701, 729, 752, 771, 796, 834, 844, 860, 882, 907, 954, 968, 1007, 1041, 1062, 1076, 1088, 1135, 1178, 1249, 1300, 1346, 1406, 1436, 1490, 1506, 1530, 1607, 3025, 3071, 3099. ^1H NMR spectrum, δ , ppm: 6.21 m (1H, H^3), 6.30 m (1H, H^4), 6.56 s (1H, CH=), 7.10 d.d (1H, H^4), 7.14 m (1H, H^5), 7.40–7.50 m (5H, H arom), 7.60 d.d (1H, H^3), 7.75 d.d (1H, H^5), 13.90 br.s (1H, NH). Found, %: C 73.37; H 4.72; N 4.66; S 11.06. $\text{C}_{17}\text{H}_{13}\text{NOS}$. Calculated, %: C 73.09; H 4.69; N 5.01; S 11.48.

(2*Z*)-3-(4,5,6,7-Tetrahydro-1*H*-indol-2-yl)-1,3-diphenylprop-2-en-1-one (XII). A mixture of 0.121 g (1 mmol) of pyrrole II, 0.206 g (1 mmol) of acetylene IV, and 3.2 g of silicon dioxide was kept at room temperature for 4 h with intermittent shaking. The reaction mixture was charged into a column packed with Al_2O_3 , elution was performed with hexane–ether mixture, 2:1. On removing the solvent a bright-orange oily substance was obtained which was ground in ethanol to produce orange crystals (0.151 g, 46%) of *Z*-isomer of pyrrole (XII), mp. 112–113°C (sublimed). IR spectrum, ν , cm^{-1} : 484, 498, 593, 607, 620, 648, 695, 716, 742, 763, 779, 817, 835, 921, 956, 1001, 1024, 1046, 1076, 1131, 1146, 1157, 1178, 1205, 1227, 1244, 1273, 1304, 1316, 1347, 1439, 1467, 1486, 1508, 1547, 1576, 1594, 1613, 2844, 2921, 2941, 3059. ^1H NMR spectrum, δ , ppm: 1.75 m (2H, $C^5\text{H}_2$), 1.82 m (2H, $C^6\text{H}_2$), 2.44 m (2H, $C^4\text{H}_2$), 2.78 m (2H, $C^7\text{H}_2$), 5.98 s (1H, H^3), 6.47 s (1H, CH=), 7.35–7.45 m (6H, $H_{m,p}$, Ph, COPh), 7.50 m (2H, H_o , Ph), 7.93 m (2H, H_o , COPh), 13.88 br.s (1H, NH). UV spectrum

(MeCN), λ , nm (log ϵ): 290 (4.48), 459 (4.37). ESR spectrum: symmetric singlet, N 2–6.10¹⁶ spin g⁻¹, ΔH 7.5 Oe, g 2.0040. Found, %: C 84.27; H 6.72; N 4.45. C₂₃H₂₁NO. Calculated, %: C 84.37; H 6.46; N 4.28.

(2Z)-3-(4,5,6,7-Tetrahydro-1H-indol-2-yl)-3-phenyl-1-(2-furyl)prop-2-en-1-one (XIII). A solution of 0.121 g (1 mmol) of pyrrole **II** and 0.196 g (1 mmol) of acetylene **V** in 2 ml of ether was mixed with 3.2 g of silicon dioxide. At slight shaking the ether within 0.5 h evaporated, and the dry mixture was heated to 75–80°C for 1.5 h till it acquired a stable dark-red color. The reaction mixture was washed with cold ethanol and then with ether. The crystals precipitated from ethanol were combined with those obtained by evaporating ether and recrystallized from 2-propanol. The yield of red-orange crystals of pyrrole **XIII** 0.295 g (90%), mp 170–171°C. IR spectrum, ν , cm⁻¹: 593, 624, 648, 660, 703, 736, 760, 787, 818, 830, 846, 883, 899, 924, 955, 1004, 1017, 1049, 1082, 1146, 1223, 1236, 1267, 1310, 1341, 1379, 1428, 1439, 1459, 1491, 1507, 1522, 1546, 1569, 1607, 2840, 2909, 2948, 3051, 3118, 3136. ¹H NMR spectrum, δ , ppm: 1.71 m (2H, C⁵H₂), 1.80 m (2H, C⁶H₂), 2.45 m (2H, C⁴H₂), 2.76 m (2H, C⁷H₂), 5.98 s (1H, H³), 6.40 s (1H, CH=), 6.50 d.d (1H, H⁴), 7.16 d.d (1H, H³), 7.44 m (3H, H_{*m,p*}, Ph), 7.48 m (2H, H_{*o*}, Ph), 7.53 d.d (1H, H⁵), 13.87 br.s (1H, NH). Found, %: C 78.95; H 6.20; N 4.37. C₂₁H₁₉NO₂. Calculated, %: C 79.47; H 6.03; N 4.41.

(2Z)-3-(4,5,6,7-Tetrahydro-1H-indol-2-yl)-1-(2-thienyl)-3-phenylprop-2-en-1-one (XIV). A solution of 0.121 g (1 mmol) of pyrrole **II** and 0.212 g (1 mmol) of acetylene **VI** in 2 ml of ether was mixed with 3.2 g of silicon dioxide. At slight shaking the ether within 0.5 h evaporated, and the dry mixture was heated to 75–80°C for 1.5 h till complete consumption of the initial reagents. The reaction mixture was washed with cold ethanol, then with ether. The ether fraction was evaporated, the residue was ground with ethanol, and pyrrole **XIV** was obtained as red-orange crystals in 0.299 g (89%) yield, mp 161–162°C (from ethanol). IR spectrum, ν , cm⁻¹: 612, 646, 668, 699, 715, 749, 768, 823, 839, 859, 914, 928, 956, 970, 1020, 1032, 1060, 1071, 1080, 1132, 1146, 1163, 1210, 1248, 1272, 1298, 1311, 1343, 1358, 1415, 1429, 1438, 1471, 1489, 1508, 1521, 1547, 1600, 2849, 2912, 2944, 3052, 3078, 3105. ¹H NMR spectrum, δ , ppm: 1.72 m (2H, C⁵H₂), 1.81 m (2H, C⁶H₂), 2.45 m (2H, C⁴H₂), 2.76 m (2H, C⁷H₂), 5.95 s (1H, H³), 6.39 s (1H, CH=),

7.07 d.d (1H, H⁴), 7.43 m (3H, H_{*m,p*}, Ph), 7.48 m (2H, H_{*o*}, Ph), 7.53 d.d (1H, H⁵), 7.68 d.d (1H, H³), 13.71 br.s (1H, NH). Found, %: C 75.21; H 6.23; N 4.08; S 9.08. C₂₁H₁₉NOS. Calculated, %: C 75.64; H 5.74; N 4.20; S 9.62.

(1Z)-1-(4,5,6,7-Tetrahydro-1H-indol-2-yl)-1-phenylpent-1-en-3-one (XV). A mixture of 0.121 g (1 mmol) of pyrrole **II**, 0.158 g (1 mmol) of acetylene **VII**, 0.003 g (1% with respect to the weight of initial reagents) of *p*-benzoquinone, and 2.8 g of silicon dioxide was kept for 2 h at room temperature. The reaction mixture was at the beginning of the process bright-green and within 2 h turned dark green (in first 15 min of the mixture self-heated by 3°C). Then the reaction mixture was washed with ethanol. On removing ethanol remained 0.232 g (83%) of resinous orange-brown residue. By extraction with hexane from the residue was isolated 0.146 g of red-orange oily substance composed of *Z*-isomer of pyrrole **XV** and acetylene **VII**, 2:1 (yield of pyrrole **XV** 34%). On storage the mixture transformed into a dark-brown powder. IR spectrum of the oily substance, ν , cm⁻¹: 614, 646, 690, 702, 759, 794, 815, 838, 930, 957, 987, 1002, 1045, 1072, 1112, 1148, 1177, 1215, 1238, 1271, 1309, 1354, 1409, 1442, 1470, 1490, 1518, 1556, 1575, 1599, 1639, 1675, 2200, 2851, 2932, 2972, 3024, 3057, 3100, 3371. ¹H NMR spectrum, δ , ppm: 1.19 t (3H, CH₃CH₂, *J* 7.3 Hz), 1.76 m (2H, C⁵H₂), 1.83 m (2H, C⁶H₂), 2.48 m (2H, C⁴H₂), 2.63 q (2H, CH₂CH₃, *J* 7.3 Hz), 2.76 m (2H, C⁷H₂), 5.83 s (1H, CH=), 5.91 d (1H, H³, *J* 1.5 Hz), 7.40 m (2H, H_{*m*}, Ph), 7.44 m (1H, H_{*p*}, Ph), 7.59 m (2H, H_{*o*}, Ph), 13.47 br.s (1H, NH). ¹³C NMR spectrum, δ , ppm: 9.55 (CH₃CH₂), 22.88 (C⁴), 23.12 (C⁶), 23.66 (C⁵, C⁷), 37.57 (CH₂CH₃), 114.99 (C ^{α}), 119.17 (C³), 121.58 (C⁹), 127.81 (C_{*o*}, Ph), 128.05 (C_{*p*}, Ph), 129.03 (C_{*m*}, Ph), 130.04 (C²), 134.90 (C⁸), 143.16 (C_{*i*}, Ph), 148.40 (C ^{β}), 200.48 (C=O).

(3Z)-4-(4,5,6,7-Tetrahydro-1H-indol-2-yl)-4-phenyl-1,1,1-trichlorobut-3-en-2-one (XVI). A mixture of 0.121 g (1 mmol) of pyrrole **II**, 0.235 g (1 mmol) of acetylene **VIII**, and 3.5 g of silicon dioxide was kept at room temperature for 20 h till it acquired stable bright orange-yellow color. The reaction mixture was washed with hexane and ether. To the residue after evaporation of the solvents was added ethanol, black precipitate containing unreacted reagents and polymeric products was filtered off. In 24 h from the ethanol solution precipitated brown-red needle crystals of pyrrole **XVI** (0.059 g, 13%), mp 113–116°C (decomp.). IR spectrum, ν , cm⁻¹: 600,

616, 658, 701, 719, 766, 796, 819, 835, 867, 926, 945, 957, 1006, 1030, 1060, 1073, 1097, 1150, 1211, 1241, 1270, 1294, 1309, 1332, 1358, 1424, 1441, 1491, 1555, 1574, 1633, 2856, 2927, 3050, 3091. ¹H NMR spectrum, δ , ppm: 1.72 m (2H, C⁵H₂), 1.82 m (2H, C⁶H₂), 2.47 m (2H, C⁴H₂), 2.77 m (2H, C⁷H₂), 6.12 s (1H, H³), 6.31 s (1H, CH=), 7.44 m (3H, H_{*m,p*}, Ph), 7.48 m (2H, H_{*o*}, Ph), 13.02 br.s (1H, NH). Found, %: C 58.58; H 4.62; Cl 29.11; N 3.57. C₁₈H₁₆Cl₃NO. Calculated, %: C 58.64; H 4.37; Cl 28.85; N 3.80.

(2Z)-1,3-Diphenyl-3-(5-phenyl-1H-pyrrol-2-yl)-prop-2-en-1-one (XVII). A mixture of 0.429 g (3 mmol) of pyrrole **III**, 0.618 g (3 mmol) of acetylene **IV**, and 10.0 g of silicon dioxide was heated for 2 h at 85–90°C. The dark-orange reaction mixture was washed with hexane to remove the unreacted reagents, and the main product was eluted with chloroform. We isolated 0.806 g (77%) of red-orange crystals of pyrrole **XVII**, mp 148–149°C (from ethanol). IR spectrum, ν , cm⁻¹: 592, 607, 618, 646, 664, 687, 715, 761, 774, 825, 907, 921, 1002, 1025, 1040, 1071, 1175, 1231, 1250, 1269, 1290, 1325, 1372, 1410, 1439, 1453, 1474, 1490, 1517, 1541, 1576, 1595, 1622, 2922, 3031, 3053. ¹H NMR spectrum, δ , ppm: 6.35 d.d (1H, H³), 6.67 s (1H, CH=), 6.71 d.d (1H, H⁴), 7.32 m (1H, H_{*p*}, PhC⁵), 7.4–7.5 m (8H, H_{*m,p*}, PhC¹, PhC⁵ i COPh), 7.5–7.6 m (2H, H_{*o*}, PhC¹), 7.85 m (2H, H_{*o*}, PhC⁵), 8.03 m (2H, H_{*o*}, COPh), 14.8 br.s (1H, NH). UV spectrum, λ , nm (log ϵ): 290 (4.48), 459 (4.37). ESR spectrum: symmetric singlet, N 2.6 × 10¹⁶ spin g⁻¹, ΔH 7.5 Oe, g 2.0040. Found, %: C 85.88; H 5.43; N 3.99. C₂₅H₁₉NO. Calculated, %: C 85.93; H 5.48; N 4.01.

(2Z)-3-Phenyl-3-(5-phenyl-1H-pyrrol-2-yl)-1-(2-furyl)prop-2-en-1-one (XVIII) was obtained similarly to adduct **XVII** from 0.286 g (2 mmol) of pyrrole **III**, 0.392 g (2 mmol) of acetylene **V**, and 6.7 g of silicon dioxide. We obtained 0.590 g (87%) of orange-red fine crystals of pyrrole **XVIII**, mp 187.5–188°C (from chloroform). IR spectrum, ν , cm⁻¹: 591, 618, 646, 665, 685, 700, 734, 750, 759, 768, 782, 827, 853, 881, 897, 920, 1004, 1015, 1041, 1055, 1073, 1085, 1148, 1177, 1220, 1267, 1291, 1320, 1366, 1404, 1439, 1450, 1464, 1490, 1514, 1540, 1568, 1614, 2923, 3066, 3126. ¹H NMR spectrum, δ , ppm: 6.32 d.d (1H, H³), 6.54 d.d. (1H, H⁴), 6.58 s (1H, CH=), 6.70 d.d (1H, H⁴), 7.26 d.d (1H, H³), 7.30 m (1H, H_{*p*}, PhC⁵), 7.4–7.5 m (7H, PhC¹, H_{*m*}, PhC⁵), 7.60 d.d (1H, H⁵), 7.83 m (2H, H_{*o*}, PhC⁵), 14.73 br.s (1H, NH). UV spectrum, λ , nm (log ϵ): 296.3 (4.48), 468 (4.45). Found, %:

C 81.01; H 5.04; N 4.09. C₂₃H₁₇NO₂. Calculated, %: C 81.40; H 5.05; N 4.13.

(2Z)-3-Phenyl-3-(5-phenyl-1H-pyrrol-2-yl)-1-(2-thienyl)prop-2-en-1-one (XIX) was obtained similarly to adduct **XVII** from 0.286 g (2 mmol) of pyrrole **III**, 0.424 g (2 mmol) of acetylene **VI**, and 7.1 g of silicon dioxide. We obtained 0.632 g (89%) of orange-red crystals of pyrrole **XIX**, mp 178–178.5°C (from chloroform). IR spectrum, ν , cm⁻¹: 590, 608, 664, 697, 719, 763, 826, 857, 905, 969, 1020, 1047, 1074, 1186, 1237, 1253, 1270, 1292, 1320, 1350, 1379, 1406, 1438, 1453, 1474, 1490, 1516, 1540, 1579, 1607, 3052, 3107. ¹H NMR spectrum, δ , ppm: 6.30 d.d (1H, H³), 6.58 s (1H, CH=), 6.67 d.d (1H, H⁴), 7.11 d.d (1H, H⁴), 7.31 m (1H, H_{*p*}, PhC⁵), 7.4–7.5 m (7H, PhC¹, H_{*m*}, PhC⁵); 7.60 d.d (1H, H⁵), 7.75 d.d (1H, H³), 7.81 m (2H, H_{*o*}, PhC⁵), 14.70 br.s (1H, NH). UV spectrum, λ , nm (log ϵ): 267 (4.20), 301 (4.50); 469 (4.44). ESR spectrum: broadened singlet, N 0.6 × 10¹⁶ spin g⁻¹, ΔH 9 Oe, g 2.0. Found, %: C 77.78; H 4.77; N 3.72; S 8.85. C₂₃H₁₇NOS. Calculated, %: C 77.72; H 4.78; N 3.94, S 9.02.

(1Z)-1-Phenyl-1-(5-phenyl-1H-pyrrol-2-yl)pent-1-en-3-one (XX). A mixture of 0.143 g (1 mmol) of pyrrole **III**, 0.158 g (1 mmol) of acetylene **VII**, and 3.0 g of silicon dioxide was kept for 70 h at room temperature till the mixture acquired stable bright orange-yellow color. The product was eluted with hexane. On evaporating the hexane the residue was red-orange oily substance which partially crystallized. It was subjected to TLC (eluent hexane–ether, 3:1). We isolated 0.099 g (33%) of orange-red crystals of pyrrole **XX**, mp 125–126°C (from hexane). IR spectrum, ν , cm⁻¹: 610, 641, 662, 689, 705, 753, 766, 795, 825, 848, 909, 932, 993, 1040, 1073, 1125, 1161, 1202, 1250, 1270, 1292, 1319, 1371, 1385, 1408, 1438, 1455, 1468, 1500, 1521, 1545, 1581, 1602, 1644, 2891, 2936, 2979, 3028, 3060. ¹H NMR spectrum, δ , ppm: 1.26 t (3H, CH₃, J 7.3 Hz), 2.70 q (2H, CH₂, J 7.3 Hz), 6.02 s (1H, CH=), 6.27 d.d (1H, H³, J 3.9, 2.4 Hz), 6.68 d.d (1H, H⁴, J 3.9, 2.0 Hz), 7.32 m (1H, H_{*p*}, Ph), 7.44 m (4H, H_{*m*}, Ph), 7.46 m (1H, H_{*p*}, Ph), 7.47 m (2H, H_{*o*}, Ph), 7.81 m (2H, H_{*o*}, Ph), 14.43 br.s (1H, NH). ¹³C NMR spectrum, δ , ppm: 9.94 (CH₃), 38.02 (CH₂), 108.98 (C⁴), 116.83 (C ^{α}), 121.60 (C³), 124.72 (C_{*o*}, Ph), 127.65 (C_{*p*}, Ph), 128.01 (C_{*o*}, Ph), 128.42 (C_{*p*}, Ph), 129.12 (C_{*m*}, Ph), 131.70 (C_{*i*}, Ph), 132.28 (C_{*o*}²), 136.77 (C⁵), 142.56 (C_{*i*}, Ph), 148.34 (C ^{β}), 201.29 (C=O). Found, %: C 82.79; H 6.81;

N 4.91. C₂₁H₁₉NO. Calculated, %: C 83.69; H 6.35; N 4.65.

The study was carried out under financial support of the Russian Foundation for Basic Research (grant no. 02-03-33017a).

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