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β-Acetyl-β-Nitrostyrenes: Structure and Use for Synthesis of Heteryl-containing Structures

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Abstract—^{1}H, IR, and electronic absorption spectroscopy and X-ray diffraction analysis were used to establish that 1-acetyl-1-nitro-2-phenyl- and 2-(*p*-methoxyphenyl)ethenes have *Z* configuration, and their 2-(*p*-*N*,*N*-dimethylaminophenyl)-substituted analog exists in chloroform-d^3 as a mixture of *Z* and *E* isomers. The reactions of *gem*-acetylnitroethenes with *N*-methylpyrrole were shown to involve alkylation at the C^2-reaction center of the heterocycle. The reactions of these nitroalkenes with hydrazine form pyrazoles and azines, with acetylhydrazine, the corresponding hydrazones (via transalkenylation), and with sodium azide, acetyl-substituted 1,2,3-triazoles.

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Geminally activated nitroethenes containing a carbonyl group as the second electron-acceptor function are preparatively available and highly reactive compounds [1, 2]. The enhanced interest in the chemistry of such polyfunctional electron-deficient compounds is due to the possibility of inclusion in their molecules of biologically active blocks (e. g., indole [3]), and also to the possibility of designing on their basis heterocyclic structures with potentially useful properties (e. g., pyrimidine derivatives [4-7], etc.). Moreover, a combination of two competing centers, an activated multiple bond and a carbonyl group, in *gem*-acetylnitrostyrenes makes them very suitable models for studying of regioselectivity problems in reactions with nucleophiles.

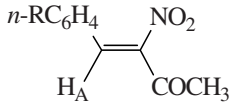
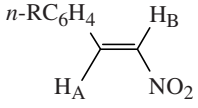
A joint analysis of ^{1}H NMR, UV and IR spectral data for β-acetyl-β-nitrostyrenes **I-III** with the use of corresponding arylnitroethenes as models made it possible to reveal the structural features of these compounds and establish, in particular, their configuration.

^{1}H NMR spectroscopy gave valuable information on the steric structure of *gem*-acetylnitroethenes. A principal criterion for the configuration of compounds **I-III** was the value of the chemical shift of the olefin proton: When the nitro group is *cis* to H_A, the signal of the latter should be shifted downfield from the corresponding signal of the *trans* isomer, due to the deshielding effect of the nitro group [8].

The ^{1}H NMR spectra of β-acetyl-β-nitrostyrene **I** and its analog **II** in $CDCl_3$ solution (Table 1) provide evidence for stereohomogeneity of these compounds; the olefin protons resonate at 7.46 and 7.32 ppm, respectively. In the ^{1}H NMR spectra of model (*E*)-β-nitrostyrenes measured in the same conditions, the olefin H_A proton signals are registered at 7.87 and 7.94 ppm. The fact that the H_A signals of compounds **I** and **II** are shifter upfield from those of *E*-β-nitrostyrenes suggests that introduction in the latter of one more electron-acceptor substituent (acetyl group) produces a configurational change and attests that compounds **I** and **II** exist in $CDCl_3$ in the *Z* form.

The ^{1}H NMR spectrum of β-acetyl-β-nitrostyrene (**III**) in $CDCl_3$, unlike those of compounds **I** and **II,** contains a double set of signals, implying that **III** exists as a mixture of isomers. There are signals of olefin protons in spectrum at 7.30 (*Z* form) and 7.90 ppm (*E* form); the *Z*/*E* ratio is ≈ 3:1.

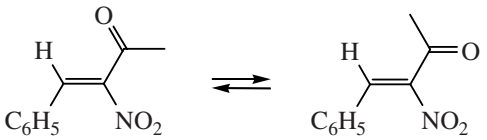
Table 1. [1]H NMR, IR, and electric absorption data for β-acetyl-β-nitrostyrenes **I–III**

Comp. no.	Compound	R	Configuration	[1]H NMR spectra ($CDCl_3$), δ, ppm (*J*, Hz)				Electronic absorption spectra (EtOH)[a]		IR spectra ($CHCl_3$), ν, cm^{-1}		
				H_A	CH_3	CH_3O [$(CH_3)_2N$]	Ar	λ_{max}, nm	ε, $l\ mol^{-1}\ cm^{-1}$	NO_2 (NOO^-)	C=O	C=C, (C=C, $C=N^+$)
I		H	*Z*	7.46	2.45	–	7.46	290	17000	1535, 1555, 1380	1700 1680	1630, 1650
II		CH_3O	*Z*	7.32	2.42	3.86	6.92, 7.43	328	23000	1550, 1350	1700	1610
IIIa		$(CH_3)_2N$	*Z*[c]	7.30	2.38	[3.05]	6.65, 7.24	410[b]	32000	1540, 1360	1690	1600
IIIb			*E*[c]	7.90	2.50	[3.10]	6.65, 7.36					
		H	*E*	7.87 (H_A) 7.60 (H_B) ($^3J_{AB}$ 14)		–	7.38	309	17200	1530, 1343	–	1640
		CH_3O	*E*	7.94 (H_A) 7.51 (H_B) ($^3J_{AB}$ 14)		3.91	6.95, 7.52	355	21000	(1320, 1300, 1258)	–	(1627, 1600)
		$(CH_3)_2N$	*E*	7.90 (H_A) 7.42 (H_B) ($^3J_{AB}$ 14)		[3.10]	6.64, 7.40	437	28700	(1320, 1298, 1267)	–	(1600)

[a] Long-wave absorption bands (λ_{max} > 280 nm) are given. [b] In the spectrum in $CHCl_3$, a long-wave absorption band (λ_{max} 414 nm, ε 28000) with a shoulder at 460 nm. [c] The *Z*/*E* ratio for compounds **IIIa** and **IIIb** is 3:1.

The electronic absorption data do not contradict the suggested configurations of the compounds under consideration (Table 1). Thus, the spectra (in ethanol) of b-acetyl-β-nitrostyrenes **II** and **III** show long-wave absorption bands characteristic of nitrostyrenes containing electron-donor substituents at the opposite end (with respect to NO_2) of the conjugated system. Acetyl substitution in *E*-β-nitrostyrenes induces a hypsochromic shift of long-wave absorption bands compared to the corresponding unsubstituted analogs [9]. Thus, the band of *E*-*p*-methoxy-β-nitrostyrene is at λ_{max} 355 nm (ε 21000), and the band of its acetyl analog, at λ_{max} 328 nm (ε 23000).

The IR spectra gave further information on the structure of compounds **I–III** (Table 1). The absorption bands characteristic of a conjugated covalently bound nitro group are observed in the IR spectrum of the simplest β-acetyl-β-nitrostyrene (**I**). Noteworthy is splitting of the absorption bands belonging to stretching vibrations of the nitro group (ν_{as} 1555, 1535 cm^{-1}), double bond ($\nu_{C=C}$ 1650, 1630 cm^{-1}) [$\Delta\nu \approx 20\ cm^{-1}$], and carbonyl group also ($\nu_{C=O}$ 1700, 1680 cm^{-1}). These observation suggests that compound **I** exists as an equilibrium mixture of the *s-cis* and *s-trans* conformers.



s-cis *s-trans*

The IR spectra of (*Z*)-β-acetyl-β-nitrostyrenes **II** and **III** that contain electron-donor substituents in the *para* position of the benzene ring differ significantly from the spectra of the corresponding model *E*-β-nitrostyrenes, which contain absorption bands of an ionized nitro group [9, 10]. In the spectra of **II** and **III** we observe absorption bands of a covalently bound nitro group (Table 1). Compounds **II** and **III,** like *E*-β-nitrostyrenes, have polarized molecules, and their polarization is much contributed by effective conjugation involving the carbonyl group.

Hence, analysis of the spectral characteristics of β-acetyl-β-nitrostyrenes **I–III** led us to conclude that these compounds prefer the *Z* form.

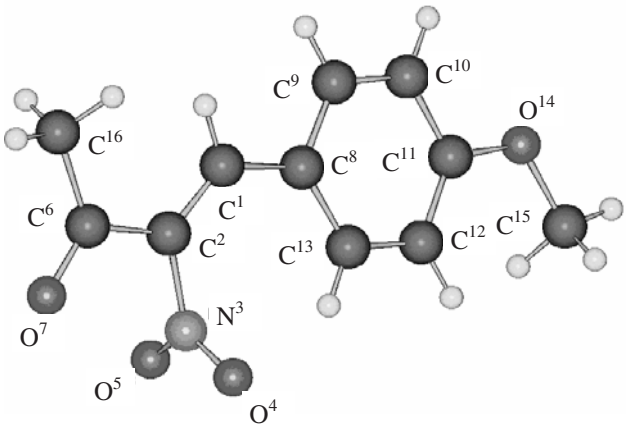
One of the β-acetyl-β-nitrostyrenes, 4-(4-methoxyphenyl)-3-nitrobut-3-en-2-one (**II**), was studied by X-ray diffraction to show that it is a *Z* isomer in crystal. Its geometry is presented in Fig.1. The principal structural parameters of molecule **II** (bond lengths and valence and torsion angles) are given in Tables 2–4.

The presented data suggest that molecule **II** in crystal is virtually planar, except that the nitro group is orthogonal to the molecular plane ($C^1C^2N^3O^4$ torsion angle 94.58°), which excludes conjugation of the nitro group with the aromatic π-system and multiple bond. Correspondingly, the C^2–N^3 bond length that equals 1.476(2) Å in β-acetyl-β-nitrostyrene (**II**) is slightly larger than in mononitrostyrene (1.451 Å). It is important that the above bond length is close to that in 1-(ethoxycarbonyl)-1-nitro-2-(*p*-nitrophenyl)ethene (1.472(3) Å [11]), where the nitro group, too, deviates from the multiple-bond plane.

According to [12], 1-acetyl-1-nitro-2-(2-thienyl) ethane which is structurally similar to compound **II**, too, has *Z* configuration in crystal, and the dihedral angle between the nitro group and ring planes is 93.3°.

We earlier showed that aromatic *gem*-acylnitroethenes actively react with CH-acids to form Michael adducts (ethyl and acetylaminoethyl malonates), transalkenylation products (malonodinitrile, ethyl cyanoacetate), substituted dihydrofurans and hexahydrobenzofurans (acetylacetone, dihydroresorcinol, dimedone) [1, 2]; with indole and its derivatives, C-adducts were obtained [3].

To proceed with research into the chemistry of nitroalkenes, we reacted β-acetyl-β-nitrostyrenes **I**–**III** with *N*-methylpyrrole, *N*,*N*-binucleophiles (hydrazine, acetylhydrazine), and sodium azide.



Molecular geometry of 4-(4-methoxyphenyl)-3-nitrobut-3-en-2-one (**II**).

Table 2. Bond lengths (*d*, Å) in molecule **II**

Bond	*d*	Bond	*d*
C^1–C^2	1.337 (2)	C^8–C^{13}	1.400 (2)
C^1–C^8	1.459 (2)	C^8–C^9	1.402 (2)
C^2–N^3	1.476 (2)	C^9–C^{10}	1.378 (2)
C^2–C^6	1.481 (2)	C^{10}–C^{11}	1.391 (2)
N^3–O^4	1.220 (1)	C^{11}–O^{14}	1.364 (2)
N^3–O^5	1.221 (2)	C^{11}–C^{12}	1.391 (2)
C^6–O^7	1.216 (2)	C^{12}–C^{13}	1.385 (2)
C^6–C^{16}	1.497 (2)	O^{14}–C^{15}	1.433 (2)

Table 3. Valence angles (ω, deg) in molecule **II**

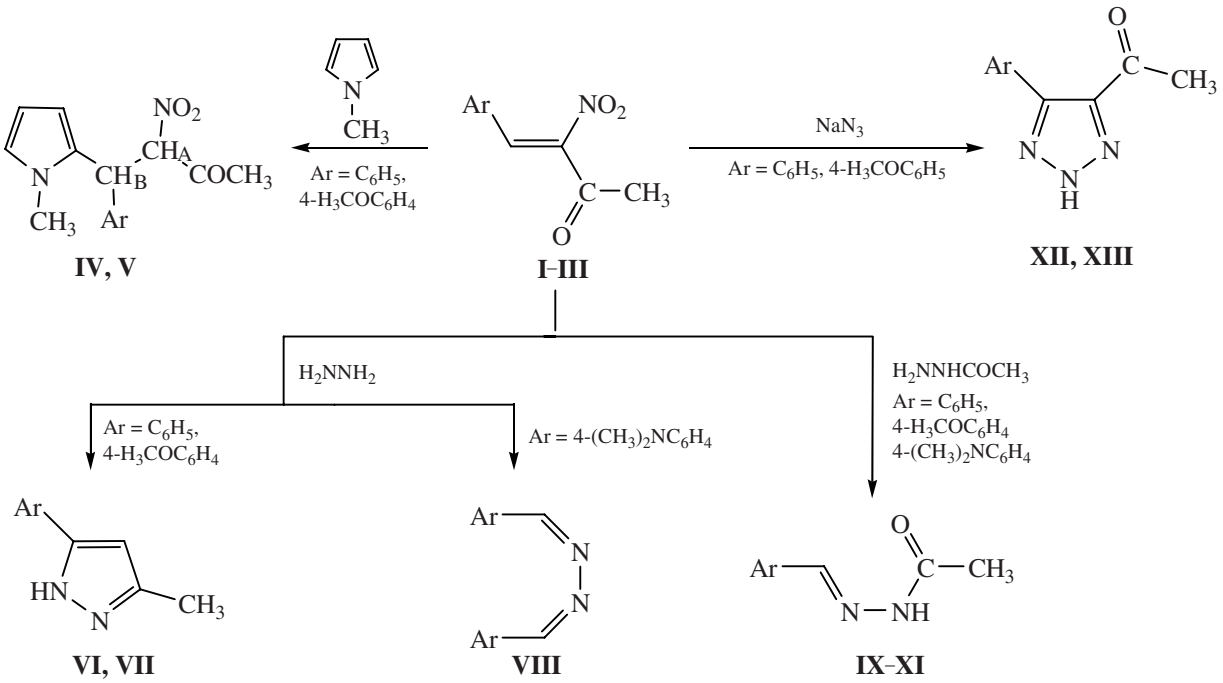
Bond angle	ω	Bond angle	ω
$C^2C^1C^8$	131.3 (1)	$C^{13}C^8C^1$	125.8 (1)
$C^1C^2N^3$	121.1 (1)	$C^9C^8C^1$	116.9 (1)
$C^1C^2C^6$	128.2 (1)	$C^{10}C^9C^8$	121.4 (1)
$N^3C^2C^6$	110.6 (1)	$C^9C^{10}C^{11}$	120.1 (1)
$O^4N^3O^5$	124.4 (1)	$O^{14}C^{11}C^{10}$	116.0 (1)
$O^4N^3C^2$	118.0 (1)	$O^{14}C^{11}C^{12}$	124.1 (1)
$O^5N^3C^2$	117.6 (1)	$C^{10}C^{11}C^{12}$	119.8 (1)
$O^7C^6C^2$	119.2 (1)	$C^{13}C^{12}C^{11}$	119.5 (1)
$O^7C^6C^{16}$	121.9 (1)	$C^{12}C^{13}C^8$	121.8 (1)
$C^2C^6C^{16}$	119.0 (1)	$C^{11}O^{14}C^{15}$	117.2 (1)
$C^{13}C^8C^9$	117.4 (1)		

Table 4. Torsion angles (τ, deg) in molecule **II**

Torsion angle	τ	Torsion angle	τ
$C^8C^1C^2N^3$	–0.03	$C^{13}C^8C^9C^{10}$	1.84
$C^8C^1C^2C^6$	–179.11	$C^1C^8C^9C^{10}$	177.68
$C^1C^2N^3O^4$	94.58	$C^8C^9C^{10}C^{11}$	–0.18
$C^6C^2N^3O^4$	–86.20	$C^9C^{10}C^{11}O^{14}$	179.17
$C^1C^2N^3O^5$	–86.47	$C^9C^{10}C^{11}C^{12}$	–1.45
$C^6C^2N^3O^5$	92.76	$O^{14}C^{11}C^{12}C^{13}$	–179.33
$C^1C^2C^6O^7$	179.47	$C^{10}C^{11}C^{12}C^{13}$	1.34
$N^3C^2C^6O^7$	0.31	$C^{11}C^{12}C^{13}C^8$	0.39
$C^1C^2C^6C^{16}$	–0.22	$C^9C^8C^{13}C^{12}$	–1.95
$N^3C^2C^6C^{16}$	–179.37	$C^1C^8C^{13}C^{12}$	177.52
$C^2C^1C^8C^{13}$	–8.83	$C^{10}C^{11}O^{14}C^{15}$	–178.01
$C^2C^1C^8C^9$	170.64	$C^{12}C^{11}O^{14}C^{15}$	2.64

Nitroethylation of pyrrole was shown to proceed in the absence of any catalytic agents and solvents and results in formation of alkylation products **IV** and **V**; this reaction is known as "substitutive addition" [13].

It should be pointed out that reactions of pyrrole with β-nitrostyrenes and their analogs are reportedly



Ar = C_6H_5 (**I, IV, VI, IX, XII**); 4-H_3CO–C_6H_4 (**II, V, VII, X, XIII**); 4-$(CH_3)_2N$–C_6H_4 (**III, VIII, XI**).

very laborious to perform, occur for a long time, and often require catalysts (ZnI_2, I_2, etc.) [14, 15].

The structure of pyrrolylnitrobutanones **IV** and **V** is proved by spectral data (Table 5). Their IR spectra show strong stretching vibration bands of unconjugated nitro (1560, 1360 cm^{-1}) and carbonyl (1740 cm^{-1}) groups. The ^1H NMR spectra of **IV** and **V** in chloroform contain double sets of signals, implying that the compounds are present as mixtures of diastereomers in 2 : 1 and 4 : 1 ratios, respectively (Table 5).

The reactions studied demonstrate the use of β-acetyl-β-nitrostyrenes as nitroketoalkylating agents for pyrrole (C^2).

According to published data, reactions of such N,N-binucleophiles as hydrazine and its derivatives with unsaturated ketones are a suitable method for preparing pyrazolidones [16], 2-pyrazolines [16, 17] and pyrazoles [18]. We found that gem-acetylnitroethenes I-III react with hydrazine ($pK_в$ 5.5 [19]) in ethanol at a small excess of *N,N*-binucleophile at room temperature in the absence of a catalyst; the products are formed in low yield and they are difficult to isolate. Significantly better results were obtained with a sixfold excess of hydrazine in the presence of *p*-toluenesulfonic acid (PTSA). In these conditions, the reactions of β-acetyl-β-nitrostyrenes **I** and **II** with hydrazine result in direct isolation (even after 30–40 min) of heterocyclization products: substituted pyrazoles **VI** (61%) and **VII** (57%).

Probably, the reaction of β-acetyl-β-nitrostyrenes **I** and **II** with hydrazine initially forms adducts by the C=C bond, as is the case with heterocyclic nitroeneketones [20]. The isolation of substituted pyrazoles **V** and **VI** suggests that the initially formed monoadducts are susceptible to further intramolecular nucleophilic addition of the NH_2 group to carbonyl, forming pyrazoline derivatives which undergo spontaneous elimination of HNO_2 to give stable pyrazole systems. Obviously, PTSA activates the carbonyl group at the stage of cyclization of linear adducts.

Evidence for the suggested structure of **VI** comes from the fact that its melting point is close to that of the earlier described sample synthesized by others methods [21, 22].

The structures of pyrazoles **VI** and **VII** were proved by ^1H NMR and IR spectroscopy. Thus the IR spectrum of substituted pyrazole **VII** contains no absorption bands of the carbonyl and nitro groups. The pyrazole NH stretching vibration band is observed at 3435 cm^{-1}. In the ^1H NMR spectrum of compound

Table 5. Yields, melting points, and spectral data of pyrrolylbutanones **IV** and **V**[a]

Comp. no.	Yield, %	mp, °C	IR spectra ($CHCl_3$), ν, cm^{-1}		^1H NMR spectra ($CDCl_3$), δ, ppm (*J*, Hz)			
			NO_2	C=O	H_A	H_B	CH_3 (N–CH_3) [O–CH_3]	Pyr (Ar)
IVa	44	68–70	1560 1360	1740	5.86 d	4.99 d	2.29 s (3.49 s)	6.09, 6.20, 6.52 (7.27 m)
					$^3J_{AB}$ 11.77 Hz			
IVb					5.87 d	5.00 d	1.86 s (3.40 s)	6.05, 6.20, 6.52 (7.27 m)
					$^3J_{AB}$ 11.03 Hz			
Va	28	88–90	1560 1360	1740	5.79 d	4.86 d	2.28 s (3.46 s) [3.80 s]	5.95, 6.04, 6.51 (6.80–7.30 m)
					$^3J_{AB}$ 11.77 Hz			
Vb					5.83 d	4.94 d	1.88 s (3.38 s) [3.74 s]	5.73, 6.16, 6.51 (6.80–7.30 m)
					$^3J_{AB}$ 11.03 Hz			

[a] Compounds **IV** and **V** were isolated as mixtures of diastereomers **a** and **b** in 1:2 and ≈3:1 respectively; isomer **a** gives upfield H_A and H_B proton signals and isomer **b** gives downfield H_A and H_B proton signals.

VII, the signals of pyrazole ring protons fall into the resonance region of benzene ring protons at 6.85–7.60 ppm. The singlets at 2.50 and 3.85 ppm belong to the CH_3 and OCH_3 groups, respectively.

No pyrazole formation is not observed in the hydrazine reaction with β-acetyl-β-nitrostyrene **III** containing an *N*,*N*-dimethylamino group in the *para* position of the aromatic ring. In this case, 4-(dimethylamino)benzaldehyde azine (**VII**) was isolated in high yield (96%). The structure of azine **VIII** was proved by its independent synthesis from the corresponding aldehyde and hydrazine. Probably, the reaction of compound **III** with hydrazine involves an Ad_N reaction (2 mol of nitroeneketone with 1 mol of hydrazine) providing a bis-adduct which undergoes cleavage with elimination of the acetylnitromethyl anion and formation of 4-(dimethylamino)benzaldehyde azine. The energetic advantage of the conjugated system in the latter product is likely to be a key factor responsible for this reaction direction; just this transformation was observed in the reaction of 1-acyl-2-(1-methylindol-3-yl)-1-nitroethenes with hydrazine [20].

gem-Acetylnitroethenes **I–III,** too, react with acetylhydrazine (pK_B 10.76 [23]) in fairly mild conditions (reaction time 1 h, solvent ethanol–benzene, room temperature) and gives rise to aromatic aldehyde *N*-acetylhydrazones **IX–XI** in yields of up to 87%. The products were identified by measuring of the melting points of their mixed samples with model samples specially synthesized from aromatic aldehydes and acetylhydrazine. Probably, the adducts of acetylhydrazine by the multiple C=C bond, formed at the first stage, do not heterocyclize (as in the case of hydrazine) but are cleaved, releasing the acetylnitromethyl anion and transforming into *N*-acetylhydrazones. This is likely to be due to the reduced basicity, steric inaccessibility of the second nucleophilic center of acetylhydrazine, high stability of the leaving finctionalized carbanion, and formation of energetically advantageous conjugated systems.

The structure of *N*-acetylhydrazones **IX-XI** is additionally proved by IR and ^1H NMR spectroscopy. Thus the IR spectrum of benzaldehyde *N*-acetylhydrazone **IX** show C=O and C=N absorption bands at 1680 and 1615 cm^{-1}. The broad absorption band in the range 3100–3300 cm^{-1} corresponds to stretching vibrations of NH-associated secondary amide group. The ^1H NMR spectrum of compound **IX** contains olefin and aromatic ring proton signals at 7.26–7.85 ppm. The singlet at 2.34 ppm corresponds to CH_3 protons, and the NH proton resonates at 10.03 ppm.

The reactions of β-acetyl-β-nitrostyrenes **I** and **II** with sodium azide proceed in DMF under comparatively mild conditions (room temperature, 2.5 h, nitroeneketone:sodium azide 1:2) and forms aryl-substituted 4-acetyl-1,2,3-triazoles **XII** and **XIII** in 94 and 91% yields, respectively. It likely that the process formally follows the 1,3-dipolar cycloaddition scheme, like reactions of others functionally substituted nitroethenes with NaN_3 [24–28].

It should be noted that compounds **XII** and **XIII** were earlier prepared in a different way, e.g. by the reaction of sodium azide with *gem*-sulfonyl-substituted unsaturated ketones, but only under more rigid conditions and in lower yields (64–70%) [29].

Thus, we showed that β-acetyl-β-nitrostyrenes react with *N*-methylpyrrole, hydrazine, and sodium azide to form nitroketenes containing an active pharmacophoric pyrrole structure, as well as substituted pyrazoles and 1,2,3-triazoles. These reactions can be used for preparative synthesis of the above heteryl-containing systems which are potentially biologically active compounds. We can mention here haemoglobin, chlorophyll, vitamin B_{12}, proline, and many medicinals (atropin, cocaine, pyrrolenitrin, etc.) containing the pyrrole ring in their molecules. Carbonyl-containing pyrazole derivatives, such as pyrazolones, are widely used as antipyretic, anesthetic, and anti-inflammatory drugs (antipyrine, amidopyrine, analgine, butadiene, etc.). Certain 1,2,3-triazoles posses antifungal, antimicrobial, and antiviral properties. For example, 5-(4-bromophenyl)- and 5-(4-nitrophenyl)-4-nitro-1,2,3-triazoles exhibit turbecularstatic and antifungal effects [25].

EXPERIMENTAL

The IR spectra were registered on an Infralum FT-02 instrument ($CDCl_3$, KBr). The UV spectra were recorded on a Specord M-40 spectrophotometer in ethanol. The ^1H NMR spectra were measured on a Bruker AC-200 (200 MHz) spectrometer ($CDCl_3$-d^1, CD_3CN-d^3) against external HMDS with an accuracy of ±0.5 Hz.

Compounds **I–III** were prepared by the procedures described in [1].

X-ray diffraction analysis of compound II. Crystals **II**: $C_{11}H_{11}NO_4$, monoclinic, space group $P2_1/c$. Unit cell parameters at –75°C: *a* 7.418(1), *b* 11.134 (1), *c* 13.613(1) **Å**, b 104.37(1)°, V 1089.2(2) Å^3, Z 4, d_{calc} 1.349 g cm^{-3}. The unit cell parameters and intensities of 23198 reflections, of which 2680 were unique (R_{int} 0.026] were measured on a Nonius KappaCCD automatic diffractometer (λMoK_α, graphite monochromator, θ ≤ 28.39°) at –75°C using COLLECT (Nonius B.V., 1998), Dirax/lsq (Duisenberg & Schreurs, 1989—2000), and EvalCCD (Duisenberg & Schreurs, 1990–2000) programs. Empirical absorption corrections were applied. The structure was decoded by a direct method using SHELXS-97 and refined using SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997). The final divergence factors were *R* 0.040 and R_W 0.105, on 2187 unique reflections with $F^2 \geq 2\sigma$.

4-(1-Methylpyrrol-2-yl)-3-nitro-4-phenylbutan-2-one (IV). *N*-Methylpyrrole, 0.133 ml, was added to 0.143 g of 3-nitro-4-phenylbut-3-en-2-one (**I**). The reaction mixture was heated to the melting point under continuous stirring, allowed to stand for 4 days in a dark place, treated with ethanol, and the precipitate was filtered off. Yield 0.09 g (44%), crystals (mixture of diastereomers in a 1:2 ratio), mp 68–70°C (from ethanol). Found, %: C 66.00; 66.02; H 5.41; 5.44. $C_{15}H_{16}N_2O_3$. Calculated, %: C 66.18; H 5.88.

4-(4-Methoxyphenyl)-4-(1-methylpyrrol-2-yl)-3-nitrobytan-2-one (V). *N*-methylpyrrole, 1.8 ml, was added to 0.442 g of 4-(4-methoxyphenyl)-3-nitrobut-3-en-2-one (**II**). The mixture allowed to stand at room temperature in a dark place. After 3 days, ethyl acetate and water (4:1) were added, and the layers were separated in a separatory funnel. The organic layer was washed with two portions of saturated sodium chloride and dried over magnesium sulfate for 1 day. The solvent was evaporated in a Petri dish, and the residue was treated with ethanol. Yield 0.16 g (28%), crystals (mixture of diastereomers in a 1:4 ratio), mp 88–90°C (from ethanol). Found, %: N 9.55; 9.48. $C_{16}H_{18}N_2O_4$. Calculated, %: N 9.27.

3(5)-Methyl-5(3)-phenylpyrazole (VI). To a suspension of 0.288 g of 3-nitro-4-phenylbut-3-en-2-one (**I**) in 2 ml of ethanol, 0.44 ml of 98% hydrazine hydrate solution and 0.07 g of *p*-toluenesulfonic acid were added. The reaction mixture was stirred at room temperature for 40 min, poured into water with ice, and cooled in a refrigerator for 3 h. The precipitate was filtered off and dried. Yield 0.145 g (61.2%), white crystals, mp 124-126°C (from 50% methanol); published data [30a]: mp 127°C (from benzine).

3(5)-Methyl-5(3)-(4-methoxyphenyl)pyrazole (VII). To a suspension of 0.332 g of 4-(4-methoxyphenyl)-3-nitrobut-3-en-2-one (**II**) in 2 ml of ethanol, 0.44 ml of 98% hydrazine hydrate solution and 0.07 g of *p*-tolunesulfonic acid were added. The reaction mixture was stirred at room temperature for 40 min and then poured into water with ice. The precipitate was filtered off and dried. Yield 0.162 g (57.4%), white crystals, mp 130–132°C (from 50% methanol). Found, %: N 14.60; 14.68. $C_{11}H_{12}N_2O$. Calculated, %: N 14.89.

4-(*N*,*N*-Dimethylamino)benzaldehyde azine (VIII) was prepared similarly from 0.351 g of 4-(4-*N*,*N*-dimethylaminophenyl)-3-nitrobut-3-en-2-one (**III**). Yield 0.214 g (96%), orange crystals, mp 240–242°C

(from carbon tetrachloride). A mixture with the sample obtained from 4-*N*,*N*-dimethylaminobenzaldehyde and hydrazine does not give melting point depression; published data [30b]: mp 250–253°C. Found, %: N 19.27; 19.20. $C_{18}H_{22}N_4$. Calculated, %: N 19.05.

Benzaldehyde *N*-acetylhydrazone (IX). To a suspension of 0.191 g of 3-nitro-4-phenyl-but-3-en-2-one (**I**) in 2 ml of benzene, a solution of 0.148 g of acetylhydrazine in 3 ml of ethanol was added. The reaction mixture was stirred at room temperature for 1 h and then poured into a Petri dish. The precipitate that formed after evaporation of the solvent was washed with benzene and filtered off. Yield 0.075 g (46%), colorless crystals, mp 126–128°C (from carbon tetrachloride). A mixture with the sample obtained by independent synthesis from benzaldehyde and acetylhydrazine gave no melting point depression.

4-Methoxybenzaldehyde *N*-acetylhydrazone (X) was prepared similarly from 4-(4-methoxyphenyl)-3-nitrobut-3-en-2-one (**II**). Yield 67%.

4-(*N*,*N*-Dimethylamino)benzaldehyde *N*-acetylhydrazone (XI) was prepared similarly from 4-(4-*N*,*N*-dimethylaminophenyl)-3-nitrobut-3-en-2-one (**III**). Yield 87%.

4-Acetyl-5-phenyl-1,2,3-triazole (XII). A mixture of 0.191 g of 3-nitro-4-phenylbut-3-en-2-one (**I**) and 0.13 g of sodium azide in 7 ml of DMF was stirred at room temperature for 2.5 h and then poured in crushed ice and acidified with 10% HCl to pH ~ 1. A day after, the precipitate was filtered off and dried. Yield 0.176 g (94%), colorless crystals, mp 111–112°C (from benzene); published data [29]: 112°C [29]. Found, %: N 22.53; 22.50. $C_{10}H_9N_3O$. Calculated, %: N 22.46.

4-Acetyl-5-(4-methoxyphenyl)-1,2,3-triazole (XIII) was prepared similarly from **II**. Yield 91%, mp 98–99°C (from benzene); published data [29]: 102°C. Found, %: N 19.41; 19.38. $C_{11}H_{11}N_3O_2$. Calculated, %: N 19.30.

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