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Features of the Reactions of β-Aryl(heteryl)-α-nitroacrylates with *N*,*N*-, *N*,*O*-, and *N*,*S*-Binucleophiles

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Abstract—The reactions of β-aryl(heteryl)-α-nitroacrylates with *N*,*N*-, *N*,*O*-, and *N*,*S*-binucleophiles proceed regiospecifically through the initial formation of the Ad_N products, among which only the product from *o*-aminothiophenol was isolated. The conditions of converting the *S*-adducts into 2-aryl(heteryl)benzothiazole were found. The *N*-adducts formed in the reaction with hydrazine, *o*-phenylenediamine, and *o*-aminophenol undergo immediately the spontaneous transformation into the linear (azine, azomethine) or heterocyclic (benzimidazole) structures.

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The conjugated nitroethenes are highly reactive substances and convenient synthons for various classes of organic compounds [1, 2].

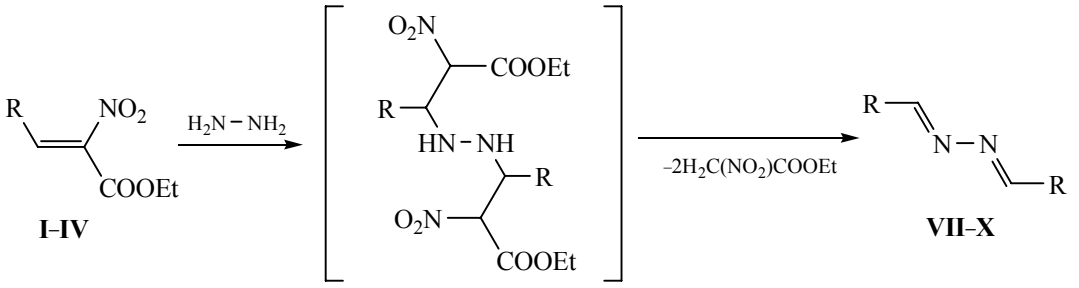
Nitroethenes containing an ester group in the *gem*-position with respect to the nitro function increase the electrophilicity of the multiple bond and have a wider range of synthetic applications. The study of β-aryl-(heteryl)-α-nitroacrylates allows to estimate of their reactivity in comparison with the simplest nitroethenes and other *gem*-substituted nitroanalogs (dinitroethenes, *gem*-halo-and *gem*-acylnitroethenes). An increased interest in the chemistry of esters of α-nitrocinnamic acids is due to the possibility to synthesize from them not only α-amino acids [3], but also the heterocyclic structures by the reactions with binucleophiles. In this case both electrophilic center of alkoxycarbonylnitroethene, the C=C bond and the ester group, may be involved into the reaction.

Analysis of the published data showed that the reactions of α-nitroacrylates with *N*-mononucleophiles were poorly studied. These reactions proceed quite peculiarly [4, 5]. For example, the esters of α-nitrocinnamic acids react with primary amine like *n*-butylamine in ethanol at reflux to form substituted isoxazoles[4]. Apparently this reaction course can be explained to the splitting of the initially formed *N*-adducts and the addition of liberated nitroacetate to the second nitroethene molecule followed by the heterocyclization of the esters of dinitroglutaric acids. The data on the reactions of α-nitroacrylates with the amino-containing binucleophiles are absent.

We studied the reactions of the esters of the α-nitrocinnamic acids and their furan- and thiophene-containing analogs **I**–**VI** with the *N*,*N*-, *N*,*O*-, and *N*,*S*-binucleophiles like hydrazine, *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol.

The reaction of α-nitrocinnamic acids esters **I**–**IV** with hydrazine proceeds under mild conditions, in ethanol at room temperature within a short time giving the corresponding aldehyde azines **VII**–**X**. In the case of the nitrocinnamate **III** containing in the *para*-position a strong electron-donor substituent, the dimethylamino group, the yield of the *p*-dimethylaminobenzaldehyde azine **IX** is close to quantitative.

Probably, the initially formed Ad_N bis-adducts liberate two molecules of the nitroacetic acid ester and convert into the corresponding azines. Apparently, the driving force of this process is the easy elimination of the resonance-stabilized anion of the nitroacetic acid ester and the energy gain obtained by the formation of conjugated systems of azines. This reaction direction has been observed previously in the reactions of hydrazine with the structurally related nitroethenes containing the acyl function in the *gem*-position to the nitro group [6, 7].



R = C_6H_5 (**I, VII**), 4-$MeOC_6H_4$ (**II, VIII**), 4-$Me_2NC_6H_4$ (**III, IX**), 4-$O_2NC_6H_4$ (**IV, X**).

Compounds **VII**–**X** were identified by the mixed melting points method for the samples obtained from the esters of α-nitrocinnamic acids **I**–**IV** and the model compounds synthesized from the corresponding aldehydes and hydrazine.

The reactions of the of α-nitrocinnamic acid esters **I** and **II** with another *N*,*N*-binucleophile, the *o*-phenylenediamine (acetic acid, 16–18°C), proceed evidently by the same way as with hydrazine: the mono-adduct converts into the bis-adduct, which easily eliminates the nitroacetic acid ester. However, in the ^{1}H NMR spectra of the obtained compounds **XI** and **XII** the signals of the azomethine protons at ~8.50 ppm are absent, but the singlet signals of the methylene protons at 5.45 and 5.38 ppm are present. Probably the initially formed linear diazomethines spontaneously underwent cyclization under the reaction conditions into 1,2-disubstituted benzimidazole system. These structures were obtained via the reaction of aromatic aldehydes and *o*-phenylenediamine (at the reagents ratio 2:1) under different conditions [8–14]: in the presence of protic and aprotic acids [8, 9], Amberlite IR-120 [10], in the ionic liquids [11], under the microwave irradiation [8], etc. Most of the authors believe that the formation of the benzimidazole structures includes the intramolecular heterocyclization of the initially formed diazomethines. The presumed route of this process has been discussed in [8]. For the samples of **XI** and **XII** mixed, respectively, with the samples obtained by the procedure [13, 14] the melting point depression was not observed.

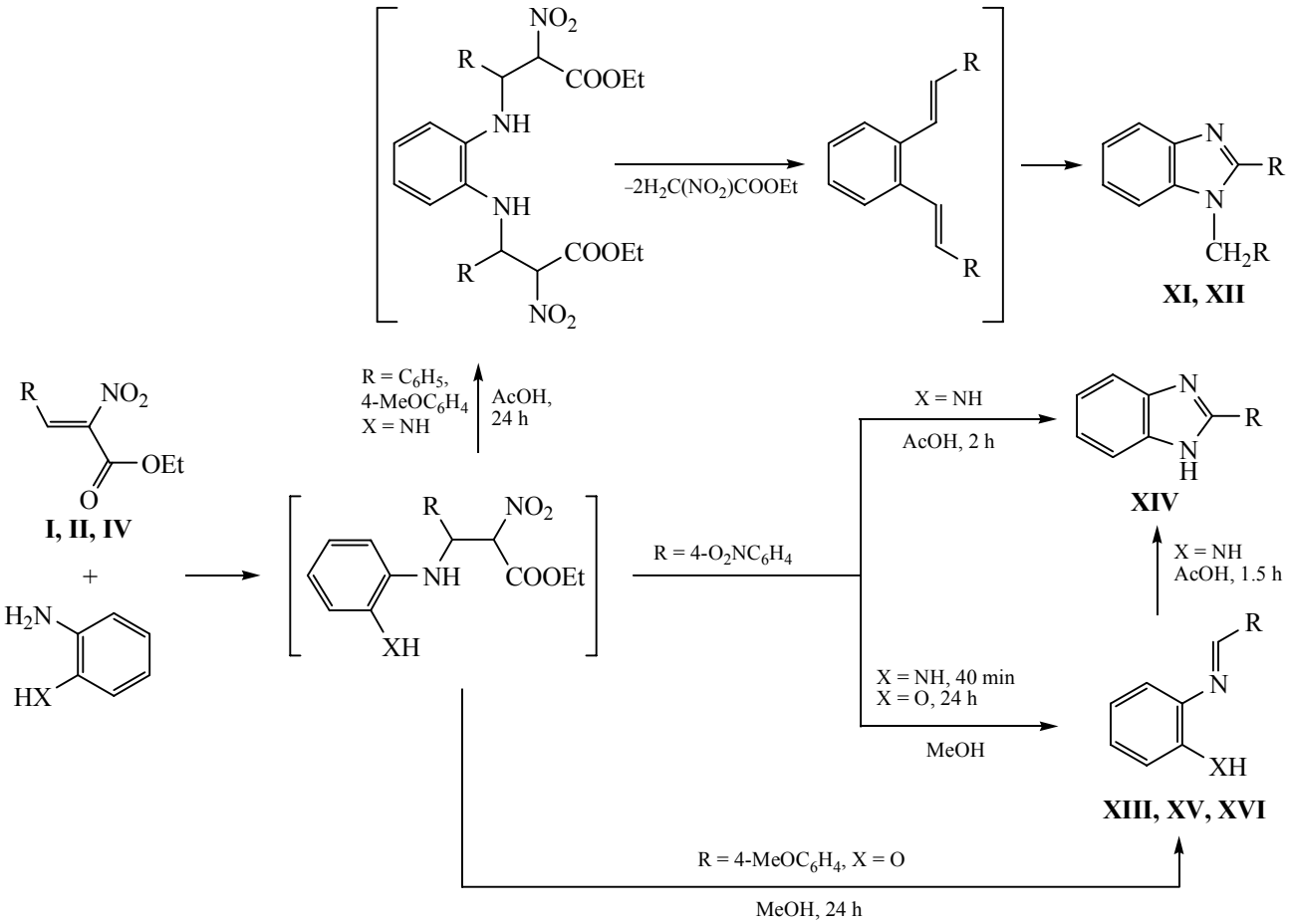
The reaction of *o*-phenylenediamine with α-nitrocinnamate **IV** containing a nitro group in the *para*-position proceeds peculiarly. The reaction occurs in the same conditions as that with nitroalkenes **I** and **II** over 2 h to yield 2-(4-nitrophenyl)benzimidazole **XIV** precipitating from the reaction mixture. The reaction of compound **IV** with *o*-phenylenediamine occurs in methanol at room temperature over 40 min to give the monoazomethine intermediate **XIII**. The latter was treated with acetic acid for 1.5 h to form also benzimidazole **XIV**.

Apparently, the intramolecular attack of the second amino group of *o*-phenylenediamine on the azomethine fragment containing a strong electron-withdrawing nitro group is faster than the intermolecular attack of this group on the C=C bond of the second nitroalkene molecule that would result in the formation of the disubstituted benzimidazoles of **XI** and **XII** type.

A possibility of α-nitroacrylates to react with a *N*,*O*-binucleophile was implemented by the example of the reaction of compounds **II** and **IV** with *o*-aminophenol. Thus, ethyl 2-nitro-3-(4-methoxyphenyl)-propenoate **II** reacts with *o*-aminophenol in methanol at room temperature over 24 h. The reaction of α-nitrocinnamate **IV** containing the nitro group in the *para*-position of the benzene ring occurs in 2 h. However, in both cases, the reactions result in the corresponding monoazomethines **XV** and **XVI** in yields of 44 and 40%, respectively. The attempt to transform compounds **XV** and **XVI** into the cyclic benzoxazole structures failed.

Due to the high propensity of the initially formed *N*-adducts to eliminate the nitroacetate, the reaction of α-nitrocinnamates with *o*-phenylenediamine and *o*-aminophenol proceeds as the tandem Ad_N–E process to form the linear azomethine or cyclic benzimidazole structures.

The reaction of α-nitroacrylates with such a representative of the *N*,*S*-binucleophiles as *o*-aminothiophenol opens interesting prospects. Due to the greater nucleophilicity of the thiol sulfur compared with the amino group it is logical to expect the formation in the first stage of *S*-adducts, which are not capable of transforming into the azomethine deriva-



R = C_6H_5 (**I, XI**), 4-$MeOC_6H_4$ (**II, XII**), 4-$O_2NC_6H_4$ (**IV, XIV**); X = NH: R = 4-$O_2NC_6H_4$ (**XIII**); X = O: R = 4-$MeOC_6H_4$ (**XV**), 4-$O_2NC_6H_4$ (**XVI**).

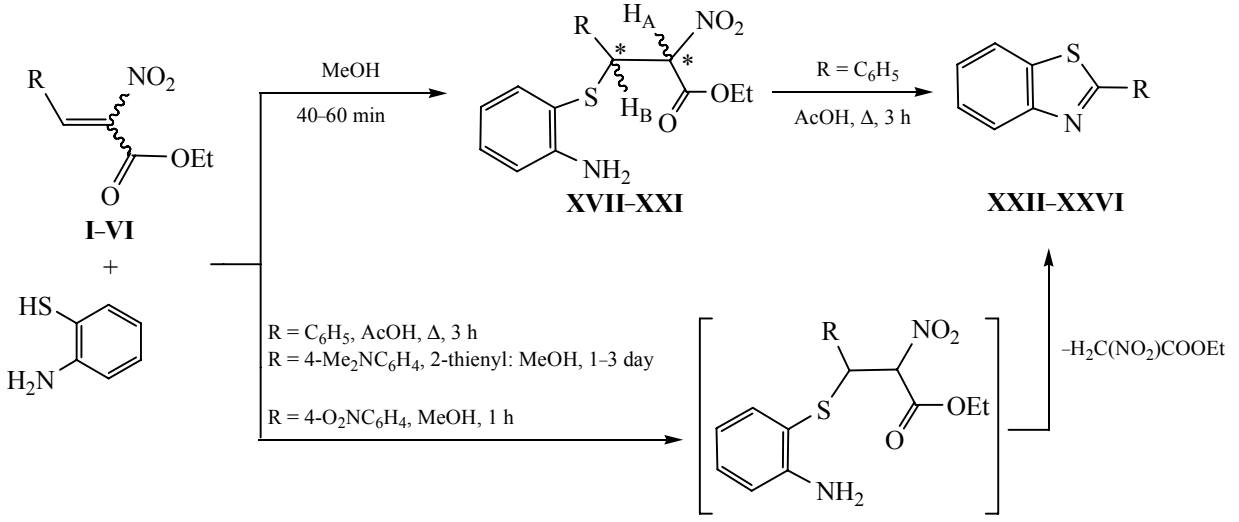
tives. Indeed, maintaining in the anhydrous methanol at room temperature (up to 1 h) α-nitrocinnamates **I**–**III** and furan and thiophene analogs **V** and **VI** with *o*-aminothiophenol results in the linear *S*-adducts **XVII**–**XXI** with yields up to 71%. In contrast to other α-nitroacrylates, the reaction of α-nitrocinnamate **IV**, containing the nitro group in the *para*-position of the benzene ring, with *o*-aminothiophenol under the same conditions without isolating the Ad_N-product results immediately in the conjugated 2-(4-nitrophenyl)benzothiazole system **XXIV**. Apparently, the process proceeds via the initial *S*-adduct formation followed by the intramolecular *N*-alkylation with releasing the nitroacetate anion. The same compound **XXIV**, but in higher yield, was obtained by reacting compound **IV** with *o*-aminothiophenol in acetic acid.

The ability of the linear adducts to cyclize was shown by converting compound **XVII** into 2-phenylbenzothiazol **XXII by** refluxing in acetic acid for 3 h. The same substance **XXII** was obtained by the one-pot reaction of α-nitrocinnamate **I** with *o*-aminothiophenol in boiling acetic acid.

The reaction of α-nitroacrylates **III** and **VI** with *o*-aminothiophenol occurs in the anhydrous methanol at room temperature within 1–3 days to give also 2-aryl (heteryl)benzothiazoles **XXIII** and **XXVI**.

The structurally related *gem*-acylnitroethenes have been previously shown to react with *o*-aminothiophenol to give the linear *S*-adducts and the cyclic dihydro-1,5-benzothiazepine structures [16, 17]. The formation of the benzothiazole derivatives instead of the benzothiazepine is probably due to the lower electrophilicity of the carbon atom of the ester function compared with the acyl group and easier cleavage of the nitroacetate anion.

The synthesized linear *S*-adducts are crystalline substances with the well-defined melting points. However, some of them, like the furan-containing compound



R = C_6H_5 (**I, XVII, XXII**), 4-$MeOC_6H_4$ (**II, XVIII**), 4-$Me_2NC_6H_4$ (**III, XIX, XXIII**), 4-$O_2NC_6H_4$ (IV, XXIV), 2-furyl (**V, XX, XXV**), 2-thienyl (**VI, XXI, XXVI**).

XX, are unstable and transform spontaneously into 2-(2-furyl)benzothiazole **XXV** with the release of the nitroacetate molecule. The composition and structure of the new linear *S*-adducts **XVII–XXI** were confirmed by the elemental analysis, IR and ^{1}H NMR spectroscopy (see the table).

Thus, in the IR spectra of compounds **XVII–XXI** there are the absorption bands of the stretching vibrations of the nonconjugated nitro group (1565, 1370–1375 cm^{-1}), ester carbonyl fragment (1750 cm^{-1}), and NH_2-group (3375–3385, 3480–3485 cm^{-1}).

The ^{1}H NMR spectra of compounds **XVII–XXI** contain the signals of all structural fragments. A double set of the proton signals indicates that these compounds in chloroform solution exist as a mixture of the diastereoisomers with the different isomers ratio (see the table). For example, in the ^{1}H NMR spectrum of compound **XVII** (**a**:**b** = 1:9) the H_A and H_B protons are registered as the doublets for **XVIIa** at 5.60 and 4.87 ppm [$^3J(H_AH_B)$ 10.99 Hz] and for **XVIIb** at 5.65 and 4.88 ppm [$^3J(H_AH_B)$ 11.60 Hz]. The protons of methyl and methylene groups in the OCH_2CH_3-fragment are registered as a triplet and a quartet at 0.94, 3.97 ppm (**XVIIa**) and at 1.35, 4.32 ppm (**XVIIb**), respectively. The amino and aromatic protons resonate at 4.12 and 6.54–7.22 ppm, respectively (see the figure).

The melting points and the spectral characteristics of compounds **XIII–XVI**, **XXII–XXVI** coincide with those of the model compounds described in the literature and obtained by other methods.

Thus as a result of the present research the main regularities of the reactions of β-aryl(heteryl)-α-nitroacrylates with the *N*,*N*-, *N*,*O*-and *N*,*S*-binucleophiles were found. The reactions include the initial regiospecific attack of the amino group (hydrazine, *o*-phenylenediamine, *o*-aminophenol) or the thiol sulfur atom (*o*-aminothiophenol) on the double C=C bond of nitroethenes. However, the reaction stopped at the stage of these products formation only in the case of the *S*-adducts. The *N*-adducts undergo spontaneous transformation into the linear (azine, azomethine) or cyclic (benzimidazole) structures via the nitroacetate molecule release. We found the conditions for the reactions of β-aryl(heteryl)-α-nitroacrylates with aminothiophenol, under which the tandem addition–heterocyclization process occurs resulting in 2-aryl(heteryl)-benzothiazole.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a Jeol JNM-ECX400A spectrometer (399.78 MHz) from chloroform-*d* solutions. The residual proton signals of the deuterated solvent were used as a standart. The IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer from solutions in chloroform (*c* 0.1–0.001 M). The elemental analysis was performed on an EA 3000 CHN Dual EuroVector analyzer.

The synthesis of the starting furan- and thiophene-containing α-nitroacrylates **V** and **VI** was performed by the methods described in [18]; the compounds **I–III**

Yields, melting points, and spectral data of *S*-adducts **XVII**–**XXI**

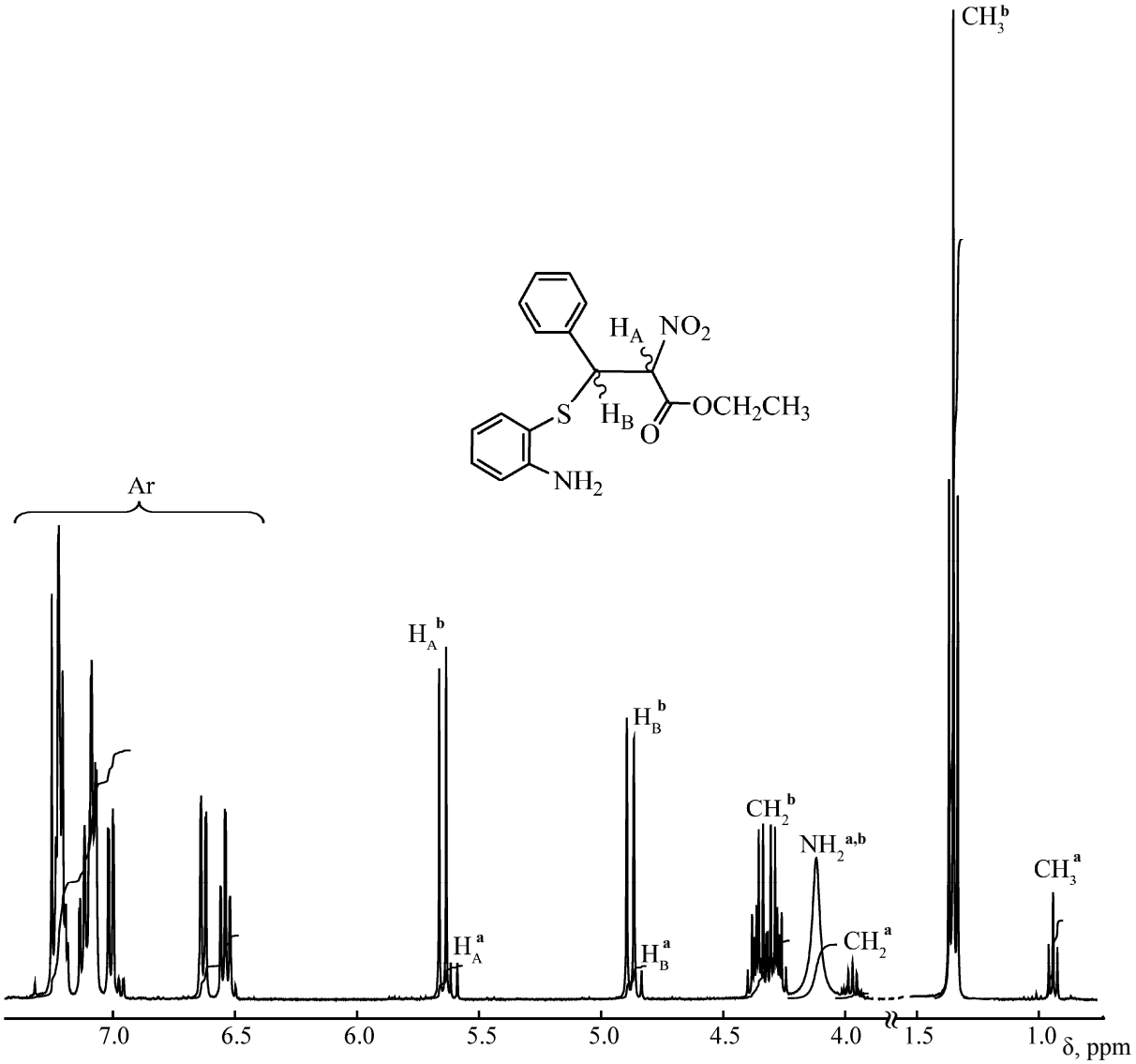
Comp. no.[a]	R	mp, °C (**a**:**b**)	Yield, %	IR sprctrum ($CHCl_3$), ν, cm^{-1}			^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)				
				NO_2	C=O	NH	H_A	H_B	OCH_2CH_3 (OCH_3) [$N(CH_3)_2$]	NH_2	Ar, Ht
XVIIa	C_6H_5	114–116 (1:9)	59	1565, 1375	1750	3375, 3480	5.60 d	4.87 d	0.94 t, 3.97 q	4.12 s	6.54–7.22 m
							J(H_AH_B) 10.99				
XVIIb							5.65 d	4.88 d	1.35 t, 4.32 q	4.12 s	
							J(H_AH_B) 11.60				
XVIIIa	4-$MeOC_6H_4$	96–98 (1:7)	53	1565, 1370	1750	3380, 3480	5.56 d	4.82 d	0.98 t, 3.98 q (3.76 s)	4.15 s	6.53–7.25 m
							J(H_AH_B) 10.99				
XVIIIb							5.60 d	4.85 d	1.34 t, 4.27 q (3.75 s)	4.15 s	
							J(H_AH_B) 11.60				
XIXa	4-$Me_2NC_6H_4$	88–90 (1:2)	66	1565, 1370	1750	3380, 3480	5.52 d	4.75 d	0.96 t, 3.96 q [2.88 s]	4.18 s	6.52–7.40 m
							J(H_AH_B) 10.68				
XIXb							5.56 d	4.79 d	1.30 t, 4.25 q [2.88 s]	4.18 s	
							J(H_AH_B) 11.29				
XXa	2-Furyl	68–70 (1:6)	71	1565 1370	1750	3385, 3485	5.60 d	4.95 d	1.11 t, 4.12 q	4.23 s	5.96–7.32 m
							J(H_AH_B) 10.38				
XXb							5.58 d	4.99 d	1.35 t, 4.35 q	4.23 s	
							J(H_AH_B) 10.99				
XXIa	2-Thienyl	84–86 (1:8)	63	1565, 1375	1750	3380, 3480	5.54 d	5.16 d	1.08 t, 4.08 q	4.22 s	6.50–7.25 m
							J(H_AH_B) 10.68				
XXIb							5.54 d	5.18 d	1.34 t, 4.34 q	4.22 s	
							J(H_AH_B) 10.70				

[a] The stereoisomers with a lower spin-spin coupling constant between the methine protons H_A and H_B are denoted as **a**, with a higher spin-spin coupling constant, as **b**.

were prepared in a similar manner, and compound **IV,** by the procedure [19].

Benzaldehyde azine (VII). To a suspension of 0.44 g (2 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** in 5 ml of ethanol was added 0.05 ml (1 mmol) of 98% hydrazine hydrate solution. The reaction mixture was stirred at room temperature for 5 h, then poured into the ice water and acidified with 10% hydrochloric acid to the neutral reaction. The formed precipitate was filtered off. Yield 0.08 g (38%), yellow crystals, mp 94–96°C (ethanol) {mp 93–94°C (ethanol) [20]}. For this sample and the sample obtained from benzaldehyde and hydrazine hydrate the melting point depression was not observed.

4-Methoxybenzaldehyde azine (VIII). To a suspension of 0.45 g (2 mmol) of ethyl 3-(4-methoxyphenyl)-2-nitropropenoate **II** in 5 ml of ethanol was added 0.7 ml (14 mmol) of 98% hydrazine hydrate solution. The reaction mixture was stirred at room temperature for 1.5 h, then poured into the ice water and acidified with 10% hydrochloric acid to the neutral reaction. The formed precipitate was filtered off. Yield 0.17 g (63%), yellow crystals, mp 162–164°C (ethanol) {mp 164–165°C (methanol) [21]}. For this sample and the sample obtained from anisaldehyde and hydrazine hydrate the melting point depression was not observed.



^{1}H NMR spectrum of ethyl 3-(2-aminophenylsulfanyl)-2-nitro-3-phenylpropanoate **XVII** (**a**:**b** = 1:9) in $CDCl_3$.

4-*N*,*N*-Dimethylaminobenzaldehyde azine (IX) was prepared similarly from ethyl 3-(4-*N*,*N*-dimethylaminophenyl)-2-nitropropenoat **III** and 98% hydrazine hydrate solution. Yield was quantitative, mp 248–250°C (ethanol) {mp 250–253°C [22]}.

4-Nitrobenzaldehyde azine (X) was prepared similarly from ethyl 2-nitro-3-(4-nitrophenyl)propenoate **IV** and 98% hydrazine hydrate solution. Yield 40%, mp 278–280°C (ethanol) {mp 297–298°C (pyridine) [23]}.

1-Benzyl-2-phenyl-1*H*-benzimidazole (XI). To a solution of 0.66 g (3 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** in 15 ml of acetic acid was added 0.33 g (3 mmol) of *o*-phenylenediamine. The reaction mixture was kept in dark for 24 h.Then the solvent was removed on a rotary evaporator, and the residue was treated with ethanol. Yield 0.31 g (72%), mp 122–124°C (petroleum ether) {mp 132°C (ethanol) [13]}. For this sample and the sample obtained from benzaldehyde and *o*-phenylenediamine the melting point depression was not observed.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzimidazole (XII). To a solution of 0.48 g (2 mmol) of ethyl 3-(4-methoxyphenyl)-2-nitropropenoate **II** in 5 ml of acetic acid was added 0.11 g (1 mmol) of *o*-phenylenediamine. The reaction mixture was kept in the dark for 24 h. Then the solvent was removed on a rotary evaporator, and the residue was treated with

ethanol. Yield 0.19 g (55%), mp 126–128°C (ethanol) {mp 127–129°C (ethanol) [14]}. For this sample and the sample obtained from anisaldehyde and *o*-phenylenediamine the melting point depression was not observed.

2-(4-Nitrobenzylideneamino)aniline (XIII). To a suspension of 0.27 g (1 mmol) of ethyl 2-nitro-3-(4-nitrorophenyl)propenoate **IV** in 5 ml of methanol was added 0.11 g (1 mmol) of *o*-phenylenediamine. After 40 min the formed precipitate was filtered off on a glass filter. Yield 0.13 g (55%), dark-red crystals, mp 140–142°C {mp 142–144°C (ethanol) [24]}.

2-(4-Nitrophenyl)-1*H*-benzimidazole (XIV). *a*. To a solution of 0.27 g (1 mmol) of ethyl 2-nitro-3-(4-nitrophenyl)propenoate **IV** in 5 ml of acetic acid was added 0.11 g (1 mmol) of *o*-phenylenediamine. The reaction mixture was kept at 16–18°C for 2 h. The formed orange precipitate was filtered off. Yield 0.12 g (48%), mp 310–312°C (ethanol) {mp 314°C (ethyl acetate), [25]}. Found N, %: 17.64. $C_{13}H_9N_3O_2$. Calculated N, %: 17.57.

b. 0.13 g (0.55 mmol) of 2-(4-nitrobenzylideneamino)aniline **XIII** was dissolved in 5 ml of acetic acid and kept in the dark for 1.5 h. The precipitate was filtered off. Yield 0.08 g (59%), mp 310–312°C. For both samples the melting point depression was not observed.

2-(4-Methoxybenzylideneamino)phenol (XV). To a solution of 0.24 g (1 mmol) of ethyl (4-methoxyphenyl)-2-nitro-3-propenoate **II** in 5 ml of methanol was added 0.11 g (1 mmol) of *o*-aminophenol. The reaction mixture was kept at 16–18°C for 24 h. Then the solvent was removed on a rotary evaporator, and the residue was treated with ethanol. Yield 0.1 g (44%), pale yellow crystals, mp 86–88°C (ethanol) {mp 89.5°C (aqueous ethanol) [26]}.

2-(4-Nitrobenzylideneamino)phenol (XVI). To a suspension of 0.53 g (2 mmol) of ethyl 2-nitro-3-(4-nitrophenyl)propenoate **IV** in 5 ml of methanol was added 0.22 g (2 mmol) of *o*-aminophenol. The reaction mixture was kept at 16–18°C for 2 h. Then the formed precipitate was filtered off on a glass filter. Yield 0.19 g (40%), pale yellow crystals, mp 165–167°C (ethanol) {mp 162–163°C (ethanol) [27]}. For this sample and the sample obtained from *p*-nitrobenzaldehyde and *o*-phenylenediamine the melting point depression was not observed.

Ethyl 3-(2-aminophenylsulfanyl)-2-nitro-3-phenylpropanoate (XVII, a:b = 1:9). To 0.44 g (2 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** was added 0.25 g (2 mmol) of *o*-aminothiophenol dissolved in 10 ml of anhydrous methanol. The reaction mixture was kept at 16–18°C for 40 min. The formed precipitate was filtered off. Yield 0.41 g (59%), mp 114–116°C (ethanol). Found, %: C 59.33; H 5.28; N 7.91. $C_{17}H_{18}N_2O_4S$. Calculated, %: C 58.94; H 5.24; N 8.09.

Ethyl 3-(2-aminophenylsulfanyl)-3-(4-methoxyphenyl)-2-propanoate (XVIII, a:b = 1:7). To 0.25 g (1 mmol) of ethyl 3-(4-methoxyphenyl)-2-nitropropenoate **II** was added 0.13 g (1 mmol) of *o*-aminothiophenol dissolved in 7 ml of anhydrous methanol. The reaction mixture was maintained at 16–18°C for 1 h. Then the solution was poured into a Petri dish and treated with ethanol. Yield 0.2 g (53%), mp 96–98°C (ethanol). Found, %: C 57.00; H 5.07. $C_{18}H_{20}N_2O_5S$. Calculated, %: C 57.43; H 5.36.

Ethyl 3-(2-aminophenylsulfanyl)-3-(4-*N*,*N*-dimethylaminophenyl)-2-nitropropanoate (XIX, a:b ~1:7) was prepared similarly from ethyl 3-(4-*N*,*N*-dimethylaminophenyl)-2-nitropropenoate **III** and *o*-aminothiophenol. Yield 66%, mp 88–90°C (ethanol). Found N, %: 10.77. $C_{19}H_{23}N_3O_4S$. Calculated N, %: 10.79.

Ethyl 3-(2-aminophenylsulfanyl)-2-nitro-3-(2-furyl)propanoate (XX, a:b = 1:6) was prepared similarly from ethyl 2-nitro-3-(2-furyl)propenoate **V** and *o*-aminothiophenol. Yield 71%, mp 68–70°C (ethanol). Found, %: C 53.08; H 4.69. $C_{15}H_{16}N_2O_5S$. Calculated, %: C 53.56; H 4.79.

Ethyl 3-(2-aminophenylsulfanyl)-2-nitro-3-(2-thienyl)propanoate (XXI, a:b = 1:8) was prepared similarly from ethyl 2-nitro-3-(2-thienyl)propenoate **VI** and *o*-aminothiophenol. Yield 63%, mp 84–86°C (ethanol). Found, %: C 51.36; H 4.51. $C_{15}H_{16}N_2O_4S_2$. Calculated, %: C 51.12; H 4.58.

2-Phenylbenzothiazole (XXII). *a*. To a solution of 0.22 g (1 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** in 7 ml of acetic acid was added 0.13 g (1 mmol) of *o*-aminothiophenol. The reaction mixture was heated for 3 h, and then the solution was poured into a Petri dish. After evaporation of the solvent the residue was treated with ethanol. The solid was filtered off. Yield 0.09 g (43%), yellow crystals, mp 110–112°C (ethanol) {mp 111–112°C [28]}.

b. 0.13 g (0.38 mmol) of ethyl 3-(2-aminophenylsulfanyl)-2-nitro-3-phenylpropanoate **XVII** was dissolved in 5 ml of acetic acid. The reaction mixture

was heated for 3 h. Then the solvent was evaporated in a Petri dish. The residue was treated with ethanol. Yield 0.03 g (38%), mp 108–110°C (ethanol). For both samples the melting point depression was not observed.

2-(4-*N*,*N*-Dimethylaminophenyl)benzothiazole (XXIII). To a solution of 0.26 g (1 mmol) of ethyl 3-(4-*N*,*N*-dimethylaminophenyl)-2-nitropropenoate **III** in 10 ml of anhydrous methanol was added 0.13 g (1 mmol) of *o*-aminothiophenol. The reaction mixture was kept at room temperature for 1 day. Then the solvent was removed on a rotary evaporator, and the residue was treated with diethyl ether. Yield 0.07 g (29%), mp 150–152°C (ethanol) {mp 154–156°C [29]}.

2-(4-Nitrophenyl)benzothiazole (XXIV). *a*. To a suspension of 0.27 g (1 mmol) of ethyl 2-nitro-3-(4-nitrophphenyl)propenoate **IV** in 5 ml of the anhydrous methanol was added 0.13 g (1 mmol) of *o*-aminothiophenol. The reaction mixture was kept at 16–18°C for 1 h. Then the solution was poured into the crushed ice, and the resulting yellow precipitate was filtered off. Yield 0.06 g (21%), mp 240–242°C (benzene) {mp 240–242°C [30]}.

b. To a solution of 0.27 g (1 mmol) of ethyl 2-nitro-3-(4-nitrophenyl)propenoate **IV** in 7 ml of acetic acid was added 0.13 g (1 mmol) of *o*-aminothiophenol. The reaction mixture was kept at 16–18°C for 2 days. Then 0.08 g of yellow crystals was filtered off. Additionally 0.07 g of the crystals of **XXIV** was isolated from the mother liquor. The overall yield is 0.15 g (59%), mp 244–246°C (benzene). For both samples the melting point depression was not observed.

2-(2-Furyl)benzothiazole (XXV). The freshly prepared crystalline compound **XX** was kept for 2 weeks at room temperature at 16–18°C. The solid gradually becomes oily. The resulting mixture was treated with ethanol. mp 94–96°C (ethanol) {mp 98°C [31]}.

2-(2-Thienyl)benzothiazole (XXVI). To a solution of 0.46 g (2 mmol) of ethyl 2-nitro-3-(2-thienyl) propenoate **VI** in 10 ml of the anhydrous methanol was added 0.25 g (2 mmol) of *o*-aminothiophenol. The reaction mixture was kept at room temperature at 16–18°C for 3 days. Then the solvent was evaporated on a rotary evaporator, and the residue was treated with ethanol. Yield 0.12 g (26%), mp 89–91°C (ethanol) {mp 91–93°C [30]}. Found N, %: 6.02. $C_{11}H_7NS_2$. Calculated N, %: 6.45.

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